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THE MICA IN ARGILLACEOUS SEDIMENTS†

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INTRODUCTION

The determination of the mineral composition[1] of a variety of soils, clays, and shales, mostly from Illinois, has revealed in many of them a constituent belonging to the mica group of minerals and somewhat similar to muscovite, heretofore referred to as the "sericite-like" mineral. Other investigators[2] have noted what is apparently the same mineral in similar sediments, describing it as resembling muscovite, but as differing from it by containing less potash and more water. It has been called "hydromica" or sericite, the latter term being used because some of its physical properties appeared to be similar to those which have been associated with the mineral sericite.

Recently Endell,[3] Hofmann, and their co-workers have described a mineral from argillaceous sediments as "glimmerton," which has the

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[1] Grim, R. E., Petrology of Pennsylvanian shales and noncalcareous underclays associated with Illinois coals: *Bull. Am. Cer. Soc.*, vol. **14**, pp. 113–119; 129–134; 170–176, 1935.

Bray, R. H., Grim, R. E., and Kerr, P. F., Application of clay mineral technique to Illinois clay and shale: *Bull. Geol. Soc. Am.*, vol. **46**, pp. 1909–1926, 1935.

Grim, R. E., and Bray, R. H., The constitution of various ceramic clays: *Jour. Am. Cer. Soc.*, vol. **19**, pp. 307–315, 1936.

Grim, R. E., Bray, R. H., and Bradley, W. F., The constitution of bond clays and its influence on bonding properties: *Trans. Am. Foundrymen's Assoc.*, vol. **7**, No. 5, pp. 211–228, 1936.

[2] Bayley, W. S., Kaolin in North Carolina with a brief note on hydromica: *Ec. Geol.*, vol. **15**, pp. 236–246, 1920.

Hickling, G., China clay, its origin and nature: *Trans. Inst. Min. Eng.*, vol. **36**, pp. 10–33, 1908–9.

Galpin, S. L., Studies of flint clays and their associates: *Trans. Am. Cer. Soc.*, vol. **14**, pp. 301–346, 1912.

[3] Endell, K., Hofmann, U., Maegdefrau, E., Über die Natur des Tonanteils in Rohstoffen der Deutschen Zement-Industrie: *Zement*, vol. **24**, pp. 625–632, 1935.

same optical and x-ray properties[4] and mode of occurrence as the "sericite-like" mineral. It is probable that the mineral described by Ross and Kerr[5] as the "potassium-bearing clay mineral" is also similar to the "sericite-like" mineral. Values given by Ross and Kerr for indices of refraction and birefringence are somewhat lower than those of the material herein studied, but the presence of small amounts of impurities, such as quartz and beidellite, would account for these variations and also for the very high silica-to-alumina ratio shown by their formula approximately representing one sample.

Thus, there is no doubt that a mineral belonging to the mica group is a common constituent of argillaceous sediments. So far as is known, no attempts have been made to study this material in detail. Frequently it is found intimately mixed with other clay minerals in a very fine particle size so that analytical data concerning it are difficult or impossible to obtain. By the use of supercentrifuge fractionation technique[6] it has now become possible to obtain the mineral in a relatively pure state in certain fractions of colloidal size, from several shales, clays, and slightly weathered tills. The purest samples have been obtained in the fraction composed of particles varying from about 0.1 micron to about 0.06 micron in diameter,[7] which has been designated as the fine colloid fraction. This paper presents the results of a detailed investigation of this purified material.

NOMENCLATURE OF THE MICA MINERAL IN ARGILLACEOUS SEDIMENTS

The question arises whether the mica mineral in argillaceous sediments should be (1) classed with some species of mica, such as muscovite, phengite, or damourite, (2) denominated as sericite, "sericite-like," "hydromica," or "glimmerton," or (3) designated by a new name.

The data herein presented show that it is not possible to designate the mineral as muscovite, phengite, or any other recognized mica species because (1) it possesses important differences in composition from those assigned to other mica species, (2) it is formed as an authigenic mineral[8] in argillaceous sediments soon after deposition from the original debris and also probably as an alteration weathering product, whereas muscovite and other species of mica have mainly a different mode of origin as igneous or hydrothermal minerals, (3) it occurs in situations different from those in which most muscovite and other mica species occur, and (4) it is found in a physical state that does not convey the usual conception of the properties of muscovite. The mineral occurs commonly in particles less than one micron in diameter, and consequently a mass of it appears unlike a mass of sheets of muscovite. Thus, it would be confusing to designate soil colloidal material by the name muscovite or some other recognized species of mica.

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[4] This similarity was determined following an interchange of material by Hofmann and Grim. X-ray analyses were made on the exchanged material by Hofmann; optical analyses by Grim.

[5] Ross, C. S., and Kerr, P. F., The clay minerals and their identity: *Jour. Sed. Pet.*, vol. **1**, p. 59, 1931.

[6] Bray, R. H., Grim, R. E., and Kerr, P. F., *Idem*, **1935**.

[7] Effective diameter as calculated from Stokes' law.

[8] Grim, R. E., *Idem*, **1935**.

Similarly, it is not desirable to class the mineral as sericite, "sericite-like," "hydromica," or "glimmerton." The use of the term sericite has been varied. As a mineral name, sericite has been loosely used for material differing from muscovite only in its physical characteristics. Some material designated as sericite has been shown to differ from muscovite by containing less potash and more water,[9] or by variations[10] in other components. Rogers[11] has suggested that the term be restricted to a low temperature hydrothermal mineral. Sericite may indicate, therefore, a white mica with certain attributes of physical properties, chemical composition or origin, depending upon the user of the term. Unavoidably such diverse usage has led to confusion so that at the present time a precise concept is not conveyed when a mineral is designated as sericite. It means only a white mica which the user of the term has not wished to class as muscovite for some reason which is usually not stated. If the term sericite were to be used for the mica in argillaceous sediments in any definite sense it would require a specific new definition on the basis of composition and occurrence which would eliminate some material previously included under it. The present confusion regarding the term sericite would be increased by placing the mica herein considered under this term.

The terms "sericite-like," "hydromica," and "glimmerton" (clay mica) are not satisfactory means of designating the material. "Sericite-like" is undesirable because of the vagueness of the significance of sericite, as discussed above. "Hydromica" implies any mica more highly hydrated then muscovite, and although the mica herein considered is more highly hydrated than muscovite, its composition differs from muscovite and all other micas in other important ways, as will be shown. Moreover, other micas differing from it in occurrence or in some phase of composition may be more highly hydrated than muscovite and are, therefore, "hydromicas." The term "glimmerton" implies nothing of composition or relation to other micas, but only a mica occurring in clays. A more specific term is needed—to indicate for example, that the clay mineral mica in argillaceous sediments is distinctive from previously named species.

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[9] Shannon, E. V., The minerals of Idaho, *U. S. Nat. Mus., Bull.* **131,** 1926.

[10] Niggli, P., Zur Zusammensetzung und Bildung der Sericite: *Schweiz. Miner. u. Petrog. Mitt.,* vol. **13,** pp. 84–90, 1933.

[11] Rogers, A. F., Sericite, a low temperature hydrothermal mineral: *Ec. Geol.,* vol. **11,** pp. 118–150, 1910.

There remains only the alternative of giving a new name to the mica occurring in argillaceous sediments, and the term *illite*, taken from the State of Illinois, is here proposed. It is not proposed as a specific mineral name, but as a general term for the clay mineral constituent of argillaceous sediments belonging to the mica group. Many additional analyses must accumulate before the limits of variation of illite are known, and therefore, before it can be specifically named. The writers favor the use of a new name at this time before all limits of variations are known for the following reasons. (1) Because of differences from other mica minerals in composition, occurrence, and origin, a new name or new names for the clay mineral mica in argillaceous sediments will be required. It will cause no confusion to apply now a new general term to this material although future analytical data may make it possible to differentiate what is here included in illite into separate species with specific names, in which case the term illite may be utilized as a group or family name. (2) Petrographic analyses of clays, soils, and shales so urgently require a name to describe this common constituent that it is believed that a new name is fully justified at this time. The additional analyses necessary for specific naming will require a considerable interval of time to accumulate. The least confusion in solving the problem will arise if the required analytical data can be gathered under a definite term.

It is probable that mica similar to that herein described may occur in argillaceous material formed as a weathering product. Although such material may not be found in sediments, the writers favor calling it illite if the material cannot be classed with recognized mica species and if it is similar to illite.

Analytical Data of Illite Purified from Illinois Material

The following analytical data are representative examples of the data obtained from a very large number of samples of purified illite from slightly weathered tills, clays and shales from Illinois which have been studied. *X*-ray and microscopic study with high magnification (1500×) indicate that samples obtained from the Maquoketa shale from Calhoun County, and from the Pennsylvanian underclay from Vermilion County (Nos. 1 and 2 of Tables 1 and 3) are the purest illite samples investigated. The data from them are, therefore, most significant. Samples 3 and 5 (Tables 1 and 3), containing admixed pigmentary limonitic material, and sample 4 containing a small amount of quartz, are included to represent the character of the information obtained from less pure material.

Some analytical properties of certain clay minerals vary with the exchangeable bases which the minerals may contain. Thus, in giving analytical data it is desirable to state the exchangeable bases contained by the analyzed material. The samples herein analyzed contain ammonia as the exchangeable base.

The very small size of the individual particles in the fine colloid fractions has made it impossible to determine all physical properties. The mineral is gray, light green, or light yellow-brown and is micaceous in habit.

By carefully drying aqueous suspensions containing the mineral, it has been possible to obtain aggregates in which the individual particles all have about the same crystallographic orientation.[12] Optical and *x*-ray measurements have been made on these aggregates which can be studied like large single flakes.

Optical data.

The optical data are incomplete because the aggregates on which the measurements were made provide scant information concerning the crystal form and orientation of the mineral. Aggregates were found permitting the determination that 2V is equal to about 5°. An occasional anomalous uniaxial figure can be found. $B_{xa}(=X)$ is nearly $=c$.

The indices of refraction in Table 1 were made using liquids which are mixtures[13] of medium Government oil ($C_{10}\pm H_{22}\pm$; $n=1.466$) and monochlor-naphthalene ($C_{10}H_7Cl$; $n=1.633$). Marshall[14] suggested, and Correns and Mehmel[15] and von Baren[16] have shown, that the indices of some clay minerals vary for different immersion liquids. Sample 1 was mounted in bromobenzene plus iodobenzene ($n=1.609$), iodobenzene ($n=1.616$), and quinoline ($n=1.625$). According to von Baren, these liquids are most active in influencing optical values. In the first two liquids, the indices of refraction remained unchanged, in quinoline they were raised slightly. It can be concluded that illite's optical properties may be slightly influenced by a few liquids. This is in agreement with the concept that the optical properties of clay minerals with relatively low base exchange capacity (see pages for exchange capacity values) are influenced to the smallest degree by immersion liquids.

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[12] Bray, R. H., Grim, R. E., and Kerr, P. F., *Idem*, **1935.**

[13] Glass, Jewell J., Standardization of index liquids: *Am. Mineral.*, vol. **19**, pp. 459–465, 1934.

[14] Marshall, C. E., The orientation of anisotropic particles in an electric field: *Trans. Faraday Soc.*, vol. **26**, pp. 173–189, 1930.

[15] Correns, C. W., Mehmel M., Über den optischen und röntgenographische Nachweis von Kaolinit, Halloysit, und Montmorillonit; *Zeits. Krist.*, vol. **94**, pp. 337–348, 1936.

[16] von Baren, F. A., Über den Einfluss verschiedener Flüssigkeiten auf den Brechungsindex von Tonmineralien: *Zeits. Krist.*, vol. **95**, pp. 464–469, 1936.

TABLE 1. OPTICAL PROPERTIES OF ILLITE AS DETERMINED ON AGGREGATES OF PURIFIED MATERIAL AT ROOM TEMPERATURE

Sample No.	1	2	3	4	5
γ	1.598	1.588	1.605	1.588	1.610
$\gamma-\alpha$	.033	.033	.035	.033	.035
sign	(−)	(−)	(−)	(−)	(−)
2V	5°±	5°±	small	small	small

1. Fine colloid fraction. Maquoketa (Ordovician) shale near Gilead, Calhoun Co., Illinois.
2. Fine colloid fraction. Pennsylvanian underclay, near Fithian, Vermilion Co., Illinois.
3. Fine colloid fraction. Slightly weathered till, IVb horizon Clarence soil, Ford Co., Illinois.
4. Fine colloid fraction. Cretaceous shale, near Thebes, Alexander Co., Illinois.
5. Fine colloid fraction. Pennsylvanian shale near Petersburg, Menard Co., Illinois.

It is well known that certain anomalous optical characteristics ("Formdoppelbrechung" and "Eigendoppelbrechung") are obtained from aggregates of uniformly oriented minute rod-shaped or flake-shaped isotropic particles when they are placed in liquids. According to Ambronn and Frey,[17] variable double refraction and uniaxial interference figures are produced when such aggregates are mounted in varied index of refraction liquids, and when the size of individual particles is small in relation to the magnitude of the wave length of light used. Biaxial figures and variable double refraction are obtained under similar conditions with anisotropic particles. As the double refraction characteristics of the illite aggregates were found to be the same when determined in liquids with *n* ranging from 1.50 to 1.70, it can be concluded that the optical values are not influenced by "Formdoppelbrechung" or "Eigendoppelbrechung."

It has been shown[18] that the indices of refraction of certain clay minerals vary with loss of water as the temperature is raised to about 200°C. Figure 1 shows that the indices of refraction of illite increase on heating to low temperatures. The values on which Fig. 1 are based were made by

[17] Ambronn, H., and Frey, A., Das Polarisationsmikroskop. *Leipzig*, **1926.**

[18] Correns, C. W., Mehmel, M., *Idem.*, **1936.**

allowing small fragments of the material placed on a glass slide to remain in an oven at a given temperature for several hours. The slide and specimen were then removed and the index was measured immediately by the immersion method. Because of the tendency of the clay minerals to take up water rapidly, and because of the influence of temperature on index liquids, the values have no high degree of accuracy. The errors would tend to reduce the observed values below the true values. Figure 1 shows also that the indices of muscovite ground to -1μ increase less than those of illite when heated to the same temperature. Only aggregates of the -1μ muscovite showing random aggregate orientation were available so that mean values alone could be determined.

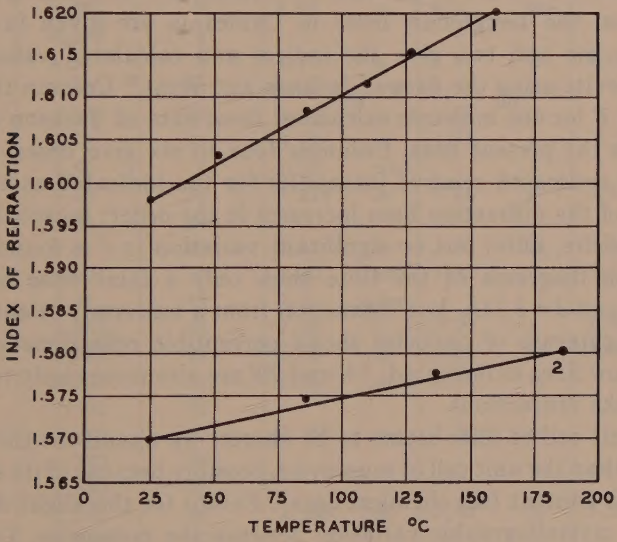

FIG. 1. Relation of index of refraction of illite and muscovite to temperature changes.
No. 1 = γ values for illite, sample 1 of Table 1.
No. 2 = mean values for -1μ muscovite.

Data for samples 1 and 2 (Table 1) obtained under the same conditions indicate that the optical properties of illite may show slight variations. Such variations are to be expected in view of the fact that the chemical composition may vary slightly (Table 3). Correns and Mehmel[19] have published results suggesting that for montmorillonite the indices of refraction increase with the Mg content. For illite sample 1 has a higher MgO content and higher indices of refraction than has sample 2. Data are not at hand to evaluate the influence of all components of clay minerals on their optical properties, so that it must not be concluded that a variation in the MgO content of illite is the only variation in composition which influences optical properties.

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[19] Correns, C. W., Mehmel, M., *Idem*, 1936.

The optical properties of illite are similar to those of muscovite except for a smaller value for 2V, and a greater variation of indices of refraction on heating to low temperatures. According to Dana,[20] 2V diminishes in micas, relatively, as the silica increases, from which it would be anticipated (see chemical composition) that 2V for illite would be smaller than for muscovite.

*X-ray data.**

Diffraction data for muscovite, illite (Sample 1 of Table 1), and sericite[21] from the Longfellow mine in California are given in Table 2. Columns one and two give the indices and calculated values of d_{hkl} for muscovite using the data of Jackson and West.[22] Column three gives values of F for one molecule calculated from data of Jackson and West and from the present data. Columns four to six give observed values of d and estimated relative intensities for the indicated samples. The breadth of the diffraction lines increases in the order: muscovite, Longfellow sericite, illite; but no significant variation in d is found. Powder diffraction diagrams of the illite show only a faint haze between $d = 4.47$Å and $d = 3.31$Å, but diffraction from a uniformly oriented flake-shaped aggregate of particles shows perceptible reflections in the $11l$ and $02l$ row lines as indicated; $13l$ and $20l$ are also more easily recognized in the flake diffractions.

The unit cell of illite seems to be shorter by about one-third of one per cent than the unit cell of muscovite, possibly because of its somewhat lower K_2O content (see chemical data). Except for this slight difference, the only crystallographic variation between the muscovite, Longfellow sericite, and illite is in particle size, or equivalently, in the perfection of crystallization.

It has been shown[23] that the chemical composition of structures of this type can vary appreciably without pronounced changes in the dif-

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[20] Dana, E. S., *Textbook of Mineralogy*, Edited by W. E. Ford. J. Wiley and Sons, New York, **1921.**

* Diffraction patterns were obtained in the laboratory of the University of Illinois through the cooperation of Professor G. L. Clark.

[21] Samples of the sericite were obtained from Prof. P. F. Kerr, Columbia University, New York, N. Y.

[22] Jackson, W. W., and West, J., The crystal structure of muscovite: *Zeits. Krist.*, vol. **76,** pp. 211–227, 1930.

[23] Marshall, C. E., Layer lattices and the base-exchange clays: *Zeits. Krist.*, vol. **91,** pp. 433–449, 1935.

TABLE 2

Muscovite calculated from Jackson and West with some additions			Muscovite observed (powder)		Sericite Longfellow mine, observed (powder)		Illite (Sample 1 of Table 1) observed (flake and powder)	
Indices	Calc. d_{hkl}	*F* for 1 molecule. Calc. for MoKα	*d*	*I*	*d*	*I*	*d*	*I*
002	9.96	15.5	9.99	s	9.96	ss	9.98	s
004	4.98	25.6	4.98	m	4.97	s	4.97	w
020	4.51	4						
110	4.48	19	4.47	ss	4.47	ss	4.47	s
$11\bar{1}$	4.45	20						
021	4.40	11						
111	4.295	9	4.29	w	4.3	ww		
$11\bar{2}$	4.215	4						
022	4.11	8	4.11	w	4.11	w	4.11	ww
112	3.965	9	3.95 db	ww	3.95 db	ww		
$11\bar{3}$	3.865	19	3.87	m	3.87	m		
023	3.73	21	3.72	m	3.75	s	3.7	ww
113	3.58	6	3.55	ww				
$11\bar{4}$	3.48	38	3.475	m	3.44	s	3.4	ww
024	3.34	24						
006	3.32	40	3.32	ss	3.32	ss	3.31	m
114	3.20	38	3.20	m-s	3.22	s	3.2	ww
$11\bar{5}$	3.11	12	3.1	ww				
025	2.987	35	2.98	s	2.99	s	2.98	w
115	2.862	29	2.86	m	2.85	m	2.84	ww
$11\bar{6}$	2.785	33	2.78	m	2.77	m		
$13\bar{1}$	2.592	35						
200	2.580	37	2.585	w	2.58	w		
116	2.570	29						
131	2.560	43						
$20\bar{2}$	2.555	46	2.560	ss	2.56	ss	2.56	s
$13\bar{2}$	2.545	38						
008	2.49	18	2.49	w	2.50	ww		
132	2.485	56						
$13\bar{3}$	2.458	25	2.46	w	2.45	w	2.44	w
202	2.441	14		ww				
$20\bar{4}$	2.387	46	2.390 db	m				
133	2.380	51	2.376		2.38	m	2.38	m
134	2.26	51						
040	2.255	18						
$22\bar{1}$	2.245	20	2.245 bd	w	2.235	w	2.24	m
041	2.24	18						
220	2.238	4						
$13\bar{5}$	2.228	10						
221	2.205	21						
$22\bar{3}$	2.179	34	2.185	w	2.185	w	2.18	w
222	2.142	19						

TABLE 2. (*Continued*)

Muscovite calculated from Jackson and West with some additions			Muscovite observed (powder)		Sericite Longfellow mine, observed (powder)		Illite (Sample 1 of Table 1) observed (flake and powder)	
Indices	Calc. d_{hkl}	*F* for 1 molecule. Calc. for MoKα	*d*	*I*	*d*	*I*	*d*	*I*
$20\bar{6}$	2.142	33	2.14	db m				
043	2.136	16	2.13		2.13	m	2.11	w
135	2.13	36						
$13\bar{6}$	2.098	29						
223	2.07	14	2.05	ww	2.05	ww		
044	2.054	14						
136	2.002	7						
0010	1.991	57	1.991	s	1.991	m	1.98	m
206	1.948	24	1.95	w	1.95	w		
$04\bar{6}$	1.865	23	1.83	ww				
138	1.756	31	1.76	w				
208	1.715	18						
0012	1.660	9						
$13\overline{10}$	1.660	2	1.654	w	1.66	w	1.65	w
$20\overline{10}$	1.657	56						
312	1.640	18	1.64	m	1.64	m	1.64	m
313	1.602	20	1.60	w	1.60	ww		
314	1.555	18	1.55	w	1.55			
1310	1.514	50	1.52	w	1.52			
2010	1.509	41						
060	1.503	65	1.504	s	1.50	s	1.50	s
$33\bar{1}$	1.498	65						
062	1.486	16						
$33\bar{3}$	1.483	15						
331	1.480	21						
0014	1.423	24						
$33\bar{7}$	1.371	6						
335	1.345	6	1.344	m	1.344	w	1.34	ww
			1.335	w	1.335	w		
260	1.30	39						
$40\bar{2}$	1.296	45						
400	1.290	51	1.295	bd w	1.295	w	1.29	m
068	1.288	26						
$33\bar{9}$	1.289	28						
337	1.287	30						
402	1.263	31						
$40\bar{6}$	1.245	26						
0016	1.245	30	1.245	bd w	1.245	w	1.24	w
264	1.242	32						

Observed diffractions were obtained with CuKα radiation.

Key: ss = very strong, s = strong, m = medium, w = weak, ww = very weak, db = discernible doublet, bd = broad.

fraction pattern. Although illite differs somewhat in chemical composition from muscovite, it is not surprising, therefore, that it should possess about the same structure.

The illite sample (Sample 1 of Table 1) does not contain diffraction lines of quartz.

Chemical data.

Computed on the basis of the analyses of the purest samples (Nos. 1 and 2 of Table 3), the composition of illite may be approximately expressed as $2K_2O \cdot 3MO \cdot 8R_2O_3 \cdot 24SiO_2 \cdot 12H_2O$. Considerable analytical work shows that the composition of the mineral is subject to some slight variation. Additional analyses of purified material must be gathered before the exact limits of the variations are known.

Table 3. Chemical Analyses of Illite*

	1	2	3	4	5
SiO_2	50.10	51.22	47.21	52.23	44.01
Al_2O_3	25.12	25.91	21.47	25.85	26.81
Fe_2O_3	5.12	4.59	10.73	4.04	11.99
FeO	1.52	1.70			
MgO	3.93	2.84	3.62	2.69	2.43
CaO	0.35	0.16	0.21	0.60	0.11
Na_2O	0.05	0.17		0.33	0.07
K_2O	6.93	6.09	5.78	6.56	4.78
TiO_2	0.50	0.53		0.37	0.64
Ign. Loss†	6.82	7.49	10.99	7.88	9.19
Total	100.44	100.70	100.01	100.55	100.03
H_2O+	7.18	7.14	6.17	7.88	8.03
H_2O-	1.90	1.45	3.80	1.13	2.33
SiO_2/R_2O_3	3.00	3.02	2.84	3.13	2.17
SiO_2/Al_2O_3	3.39	3.36	3.51	3.43	2.79

1. Fine colloid fraction, Maquoketa (Ordovician) shale, near Gilead, Calhoun County, Ill.
2. Fine colloid fraction, Pennsylvanian underclay, near Fithian, Vermilion County, Ill.
3. Fine colloid fraction, slightly weathered till, IVb horizon of Clarence soil, Ford County, Ill.
4. Fine colloid fraction, Cretaceous shale, near Thebes, Alexander County, Ill.
5. Fine colloid fraction, Pennsylvanian shale, near Petersburg, Menard County, Ill.

* Analyses 1, 2, 4 and 5 were made under the supervision of O. W. Rees, Associate Chemist, Illinois State Geological Survey; analysis 3 was made under the supervision of R. H. Bray.

† The loss on ignition values for samples 1, 2, 4 and 5 are based on material dried to 110°C.; for sample 3 it is based on air dried material.

It is noteworthy that illite has a SiO_2 to R_2O_3 ratio of about 3. This ratio higher than 2, which is generally characteristic of most mica, is not the result of admixed quartz or other minerals, such as pyrophyllite, with high SiO_2 to Al_2O_3 ratios, as the *x*-ray and optical analyses of samples 1 and 2 show that these samples consist of a single mineral. The MgO and FeO (MO) content are of sufficient magnitude and uniformity to require a place in the formula. The K_2O and H_2O contents, which are relatively low and high, respectively, for micas, are also noteworthy.

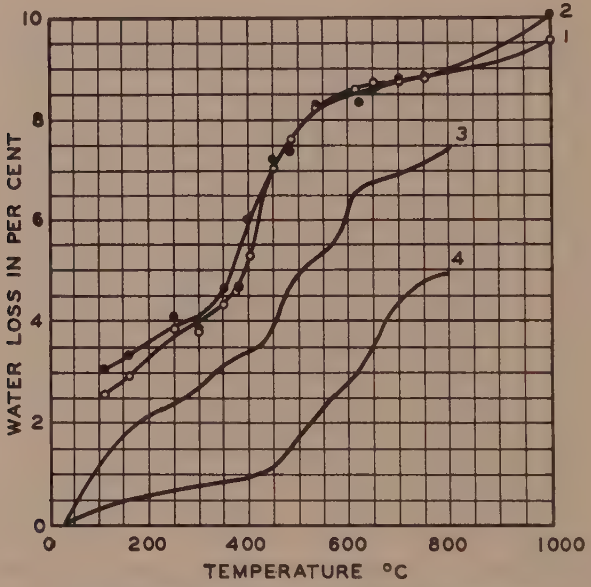

FIG. 2. Dehydration curves of illite and muscovite.
No. 1—Sample 1 of Table 1.
No. 2—Sample 2 of Table 1.
No. 3—Very finely ground muscovite.
No. 4—−100 mesh muscovite (coarser than 3).
Curves 3 and 4 after Kelley, Jenny and Brown; *Soil Sci.*, 1936.

Samples 3, 4 and 5 are less pure than 1 and 2. Samples 3 and 5 contain admixed limonitic material, and sample 4 contains quartz. The presence of these constituents must be recognized in considering the significance of the analyses of the samples.

Dehydration data.

Dehydration curves (Fig. 2) obtained from illite resemble more closely the curve for very finely ground muscovite than that of −100 mesh muscovite or those of other clay minerals.[24] Dehydration data for other micas are not available for comparative study.

Kelley, Jenny, and Brown[25] have recently shown that very fine grinding of various hydrous minerals tends to shift the inflection point to a lower temperature and to apparently reduce the crystal lattice water with the difference appearing as adsorbed water. This effect is shown by their curves for −100 mesh muscovite and for the same mineral very finely ground (Fig. 2). They have concluded that "differences in the inflection points do not necessarily signify different lattices but may be the result merely of variations in particle size." It follows that dehydration curves should not be used as diagnostic characteristics of minerals unless particle size is considered. Until dehydration data can be obtained for illite of varying particle size, the dehydration characteristics of the mineral and their value in identifying it cannot be determined fully.

TABLE 4. WATER LOSS DETERMINATIONS OF ILLITE*

Temperature °C.	Water loss in per cent	
	Sample 1	Sample 2
110	2.60	3.03
160	2.92	3.41
250	3.82	4.12
300	3.63	3.84
350	4.45	4.62
375	4.62	4.62
400	5.37	6.01
450	7.03	7.24
485	7.56	7.47
530	8.37	8.31
615	8.54	8.41
650	8.74	8.62
700	8.74	8.79
750	8.77	8.79
1000	9.60	10.14

* Determinations made under the supervision of O. W. Rees, Associate Chemist, Illinois State Geological Survey. Location of samples given in Tables 1 and 3.

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[24] For dehydration curves of other clay minerals see Ross, C. S., and Kerr, P. F., P.P. **165E,** *U.S.G.S.*, 1930; Endell, K., Hofmann, U., and Maegdefrau, E., *Zement*, vol. **24,** 1935; Kelley, W. P., Jenny, H., and Brown, S. M., *Soil Sci.*, vol. **41,** 1936.

[25] Kelley, W. P., Jenny, H., and Brown, S. M., Hydration of minerals and soil colloids in relation to crystal structure: *Soil Sci.*, vol. **41,** pp. 259–274, 1936.

Base-exchange data.

Base-exchange capacity values (Table 5) obtained on samples of illite range from about 20 to 40 milliequivalents per 100 grams. These values are lower than the value (about 50 milliequivalents per 100 grams) assigned by Hofmann, Endell[26] and their coworkers to "glimmerton" which is similar to illite. Base-exchange capacity varies with particle size so that this property should be expressed as ranging between limits. Magnitude rather than specific values are important because of variations in particle size, and also because of variations due to slight differences in composition.

TABLE 5. BASE-EXCHANGE CAPACITY

Sample No. (location Table 1)	1	2	3	4	5
Inorganic base exchange capacity in milliequivalents/100 grams	20.5	35.5	33.0	30.0	21.6

In previous reports[27] the question has been raised as to whether illite (the "sericite-like" mineral) has low base-exchange capacity or no base-exchange capacity. If no base-exchange capacity is assigned to illite in the samples studied, the base-exchange capacity shown by the samples (Table 5) can only be explained by the presence in each sample of a second mineral with high exchange capacity. Assuming for an admixed mineral a base-exchange capacity even of 100 (a high value for montmorillonite which possesses the highest exchange capacity of the clay minerals), the quantity necessary to yield the capacities would be appreciable. As already noted, *x*-ray and optical data reveal no constituent in the samples other than illite, except quartz and limonite in Nos. 3, 4, and 5, and these minerals would tend to decrease rather than increase base-exchange capacity values. Theoretical reasons[28] have been presented showing that the micas should possess base-exchange capacity. In the present research, exchange capacity values of the same order of magnitude shown for illite have been obtained from pure crystalline muscovite after grinding it to a diameter of about 1 micron, the ground material retaining the *x*-ray diffraction pattern characteristic of muscovite.

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[26] Endell, K., Hofmann, U., and Maegdefrau, E., Über die Natur des Tonanteils in Rohstoffen der Deutschen Zement-Industrie: *Zement*, vol. **24**, pp. 625–632, 1935.

[27] Grim, R. E., and Bray, R. H., *Op. cit.*, **1936.**

Grim, R. E., Bray, R. H., and Bradley, W. F., *Op. cit.*, **1936.**

[28] Van der Meulen, J. B., Relation between the phenomena of cation exchange with silica-alumina complexes and their crystal structure: *Rec. trav. chim.*, vol. **54**, pp. 107–113, 1935.

Relation of Illite to Other Micas

The analytical data provide conclusive evidence that illite is a member of the mica group of minerals and somewhat similar to muscovite. Its optical values agree with those for muscovite, except for a smaller value for 2V, and a greater variation of indices of refraction on heating to low temperatures. Illite and muscovite yield diffraction patterns with lines having the same spacings. The former mineral may be distinguished, however, by the greater width of the lines. The mineral can be differentiated from muscovite on the basis of its chemical composition because of a higher SiO_2 to R_2O_3 ratio, a higher SiO_2 to K_2O ratio, a higher R_2O_3 to K_2O ratio, an appreciable content of MO (mainly magnesia), and a higher H_2O content.

On the basis of composition, illite is more nearly similar to the phengite variety of mica than to muscovite. The term phengite has been used for white micas whose analyses suggest a higher SiO_2 to R_2O_3 ratio than 2. Also the presence of MgO in phengite has been noted. Formulae assigned to phengite ($K_2O\cdot(Mg, Fe)O\cdot 2Al_2O_3\cdot 7SiO_2\cdot 2H_2O$ by Winchell;[29] $K_2O\cdot 2Al_2O_3\cdot 6SiO_2\cdot 2H_2O$ by Tschermak;[30] $K_2O\cdot RO\cdot 2Al_2O_3\cdot 6SiO_2\cdot 2H_2O$ by Hallimond)[31] do not agree, particularly in their SiO_2 to K_2O ratios, with the analyses of illite (Table 3). A search of the literature revealed analyses 1 and 2 (Table 4) of phengite most nearly like the compositions given in Table 3. It is evident that even these specially selected analyses are not closely similar to those of illite, and, therefore, there is no justification, on the basis of composition, for designating the mineral studied as phengite.

The deep red mica from the manganese mines of St. Marcel in Italy named alurgite by Breithaupt and analyzed by Pennfield,[32] and mariposite from the Josephine mine, Bear Valley, California, analyzed by Hillebrand,[33] which Schaller[34] has shown to be the same mineral, is similar in some respects to illite. The analyses (Table 6) show important differences, however, in the H_2O and K_2O values. There is also an essential difference in the mode of occurrence.

Schwartz and Leonard[35] described a micaceous alteration product of

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[29] Winchell, A. N., *Idem*, **1929.**

[30] Tschermak, G., Die Glimmergruppe, *Zeits. Krist.*, vol. **3**, pp. 122–167, 1879.

[31] Hallimond, A. F., On the chemical classification of the mica group: *Mineral Mag.*, vol. **20**, pp. 305–318, 1925.

[32] Pennfield, S. L., On some minerals from the manganese mines of St. Marcel in Piedmont, Italy: *Am. Jour. Sci.*, 3rd Ser., vol **46**, p. 288, 1893.

[33] Hillebrand, W. F., Mineralogic Notes: *Bull.* **167**, *U.S.G.S.*, p 74, 1900.

[34] Schaller, W. T., Mineralogic Notes, Series 3; *Bull.* **610**, *U.S.G.S.*, pp. 139–140, 1916.

[35] Schwartz, G. M., and Leonard, R. J., Alteration of spodumene in Etta Mine, Black Hills, South Dakota: *Am. Jour. Sci.*, 5th Ser., vol. **11**, pp. 257–264, 1926.

TABLE 6. CHEMICAL ANALYSES OF MICAS RESEMBLING ILLITE

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	52.28	58.90	46.54	45.72	46.58	40.79	53.22	56.79	47.29	53.47	48.96	47.05
Al_2O_3	23.56	25.28	30.39	37.17	37.46	29.98	21.19	25.11	31.31	32.36	30.96	34.90
Fe_2O_3		2.30	4.42	2.18	0.80	8.07	1.22	0.63	1.19	0.79		1.50
FeO	5.76		2.98			2.48		0.92	0.37	0.42	0.24	
MgO	2.43	1.49	0.94	2.00	1.16	2.71	6.02	3.29	2.38		1.97	1.95
CaO	0.65	0.65	0.35	0.05	tr	0.45	—	0.07	0.69	0.17	0.26	
Na_2O		1.37	1.44	1.44	0.64	0.38	0.34	0.17	0.88	0.44	1.65	7.96
K_2O	9.52	5.73	5.57	6.69	6.38	3.47	11.20	8.92	4.07	7.68	8.47	
TiO_2						1.28	—	0.18				
CrO_3							0.87	—				
MnO							0.18			0.12		
F			0.58								1.04	1.45
Ign. loss	5.94	4.14	5.31	6.79			5.75	4.72		4.07	3.83	4.07
Total	100.44	99.86	98.52	102.04			99.99	100.80			99.38	98.88
H_2O+					6.06	9.34			9.92			
H_2O-					0.30	1.20			1.88			
SiO_2/R_2O_3		3.75	2.38	2.02	2.09	1.97	4.10	3.78	2.50	2.76		
SiO_2/Al_2O_3	3.77	3.96	2.61	2.09	2.12	2.31	4.24	3.84	2.57	2.81		

1. Phengite from Wildschaptachtal. *Doelter's Handbuch der Mineralchemie*, **2,** Abt. 2, p. 428, 1914.
2. Phengite from Witticbes Tal. *Doelter's Handbuch der Mineralchemie*, **2,** Abt. 2, p. 428. 1914.
3. Secondary muscovite, from Epprechstein, *Doelter's Handbuch der Mineralchemie*, **2,** Abt. 2, p. 426, 1914.
4. Damourit, from Fen. Norway. *Doelter's Handbuch der Mineralchemie*, **2,** Abt. 2, p. 422, 1914.
5. Sericite, Carroll-Driscoll mine, Idaho, from E. V. Shannon, *Bull.* **131,** *U. S. Nat. Mus.*, p. 367, 1926.
6. Hydromica, North Carolina, from W. S. Bayley, *Ec. Geol.*, vol. **15,** pp. 236–246, 1920.
7. Alurgite, Manganese mines of St. Marcel, in Piedmont, Italy, from S. L. Pennfield, *Am. Jour. Sci.*, vol. **46,** pp. 288–295, 1890.
8. White mariposite, Josephine mine, Bear Valley, California, from W. L. Hillebrand, *Bull.* **167,** *U.S.G.S.*, p. 74, 1900.
9. Secondary mica, Etta mine, S. Dakota, from G. M. Schwartz and R. J. Seward, *Am. Jour. Sci.*, vol. **11,** p. 262, 1926.
10. Secondary mica, Branchville, Conn., from G. J. Brush and E. S. Dana, *Am. Jour. Sci.*, vol. **20,** p. 274, 1880.
11. Gilbertite, from Ehrenfriedersdorf, *Dana's System of Mineralogy*, p. 618, **1914.**
12. Margarodite, from Zillerthal, *Dana's System of Mineralogy*, p. 618, **1914.**

spodumene from Etta mine, South Dakota, which has values for K_2O, MgO, and H_2O approaching those of illite. It has, however, the SiO_2 to Al_2O_3 ratio of muscovite and is believed to be of hydrothermal origin. Earlier Brush and Dana[36] described an alteration product of spodumene from Branchville, Connecticut, which probably had the same origin as the material from Etta. Except for a slightly higher silica value (Table 6), which was interpreted as indicative of a small amount of free silica, the analysis corresponds to the formula for muscovite.

The names damourite, gilbertite, and margarodite have been given to secondary micas of the muscovite type. Available chemical analyses of these minerals (Table 6) are notably different from those of illite (Table 3). Also, damourite, bilgertite, and margarodite appear mainly to have resulted from hydrothermal alteration.

The mineral described as sericite by Shannon[37] from gouge from the Carroll-Driscoll mine in Idaho (No. 5, Table 6), possesses optical and *x*-ray characteristics similar to those of illite. Chemically, however, there are important differences, particularly in the SiO_2 to Al_2O_3 ratio.

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[36] Brush, G. J., and Dana, E. S., Spodumene and the results of its alteration: *Am. Jour. Sci.*, 3rd Ser. vol. **20,** pp. 257–285, 1880.

[37] Shannon, E. V., The Minerals of Idaho: *U. S. Nat. Museum, Bull.* **131,** 1926. A sample of Shannon's original material was kindly furnished us for *x*-ray analysis. For this courtesy we are indebted to the U. S. Nat. Museum and Dr. W. F. Foshag, Curator of Mineralogy.

ORIGIN OF THE MARCASITE SINK-HOLE DEPOSITS OF CENTRAL MISSOURI

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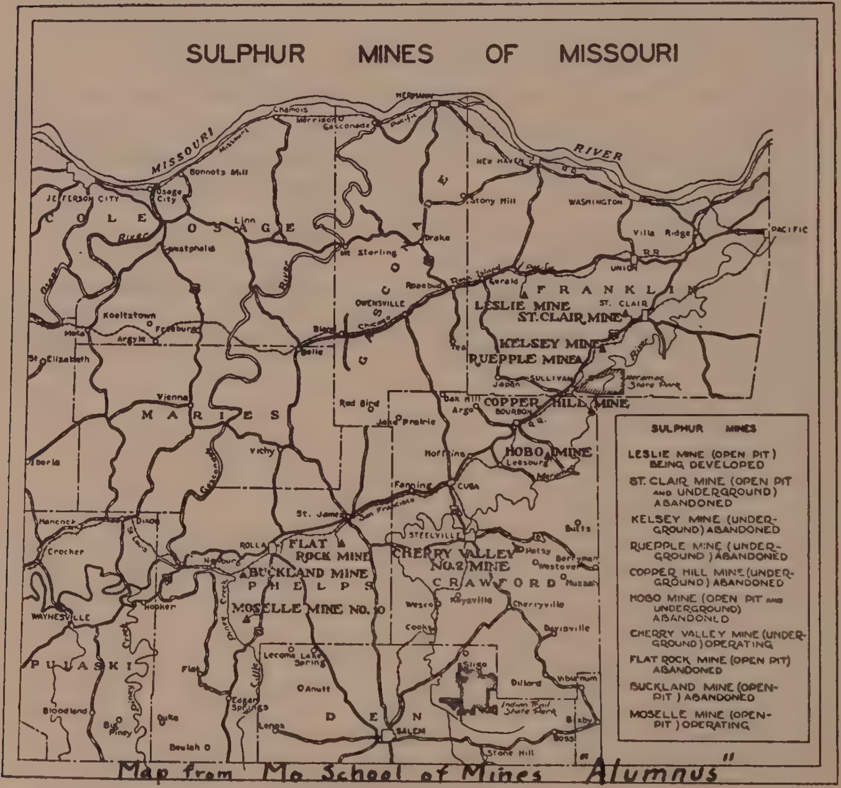
There are ten known deposits of marcasite (and pyrite in small quantities) in sink-holes in Franklin, Crawford, and Phelps counties in the northeastern part of the Missouri Ozarks, and others probably exist, either still uncovered by erosion or in connection with unmined hematite deposits of filled sinks. Only two mines, the Moselle mine, No. 10, near Rolla, and the Cherry Valley mine, east of Steelville (Fig. 1), were operating in 1936. All the deposits are associated with former hematite mines. The sulfides are mined by underground or open-cut methods, occasionally by both methods at the same deposit. As the sulfides are sold for their sulfur content, the producers try to maintain a minimum of 45 per cent S in their ore, which may average 49 to 50 per cent.

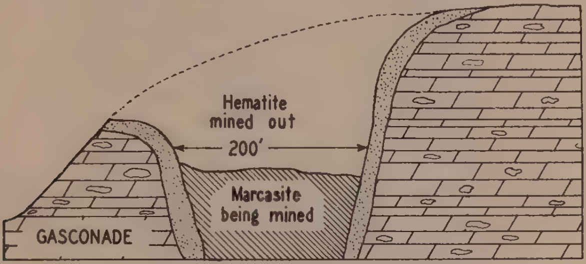


Map from Mo School of Mines "Alumnus"

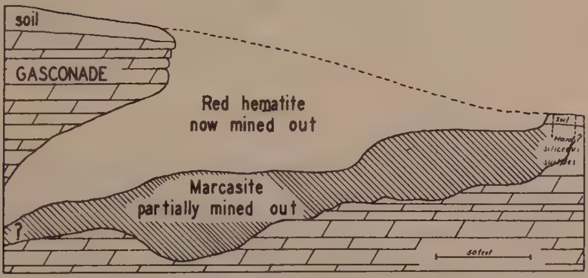
Fig. 1. Marcasite (Sulfur) Mines of Missouri.

MODE OF OCCURRENCE OF THE ORES

The sulfides occur in the lower part of sink-holes (Fig. 2), the upper part of which was originally filled with iron ore, now mined out. These sink-holes rarely exceed 500 feet in their greatest dimension and are usually 100 to 300 feet across. They may be rudely circular but more commonly are elliptical or irregular in outline. The sulfides are usually 10 to 30 feet thick, but greater thicknesses have been estimated (for example, 100 feet in Scotia mine, No. 1, Crawford County).[1] The overlying hematite ore was commonly less than 100 feet thick, but in the Ruepple mine, near Stanton, an inclined ore body was followed to a depth of 320 feet. The sulfide ore body in this mine was at a higher level than the bottom of the iron ore as it was reached through a shaft 268 feet deep.



2a - Sketch of sink-hole sulfide-hematite mine.



2b-Sketch of the Leslie, Mo. Sulfide-Hematite Mine as it is today.

FIG. 2. Sulfides in the lower part of sink-hole hematite deposits.

The sulfide ore bodies are essentially flat, but have an uneven contact with the country rock on all sides. Locally, the ores grade into the wall rock, but usually the contact is sharp. The contact with the hematite above was also uneven; at any rate, as far as can now be determined.

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[1] Crane, G. W., Iron Ores of Missouri: *Mo. Bur. Geol. and Mines*, vol. **10**, p. 219, 1912.

The deposits occur in the Gasconade (dolomite) and Roubidoux formations (both Ordovician). In the Ruepple mine, the sulfides may occur in the Van Buren (base of the Ordovician) for they apparently occur below the basal member (the Gunter sandstone) of the Gasconde. The stratigraphic range may be 500 feet, but is usually less. Where the ores occur in the upper part of the Gasconade, blocks of Roubidoux sandstone may be found along the sides of the deposit (Fig. 2a) or even within the ore. These represent blocks that were let down into the Gasconade during the formation of the sinks and galleries.

The Gasconade and Roubidoux formations normally dip gently to the northwest. Minor departures from this occur throughout the region, but the most noticeable variations are in local areas that show the results of settling associated with the sink or cavern structure. The Gasconade (300± feet thick) was the seat of most of the solution work, which developed galleries and shafts throughout the formation. Where these features reached the comparatively insoluble Roubidoux (125± feet thick) above, they were necessarily extended laterally beneath it, finally causing its collapse into the Gasconade. These collapsed portions of the Roubidoux lie at all angles within the sinks and dip steeply inward along their margins. No sandstone is found within or around some sink-holes, either having been entirely replaced or the sink-holes having developed wholly within Gasconade beds.

Description of the Minerals

The sulfide ores consist overwhelmingly of marcasite,[2] with only subordinate amounts of pyrite. No other sulfides have been identified by the writer, but the presence of metallic copper in the mine waters of the Ruepple mine indicates that the ores probably contain traces of some copper mineral, possibly chalcopyrite. Quartz, containing limonite as a coloring material, occurs sparingly as the only other mineral in the ores.

The marcasite is a typical metacolloid having reniform, botryoidal (fig. 3), mammillary, and rod-like structures, aggregates of which commonly assume beautiful plumose and feathery radiating forms (Fig. 4). Stalactitic structures (Fig. 5) are common in some mines. The marcasite also occurs massive, as a fine granular powder, and in druses and large (maximum, 2 cm. across) crystals. Some of the crystals show twinning. Coxcomb structures, such as those so well developed in the Tri-State district, are extremely rare. The metacolloidal structures are normally fibrous. These fibers are so small in some solid mammillary ores that

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[2] It is not improbable that some of the marcasite has inverted to pyrite, but the material examined by the writer was marcasite.

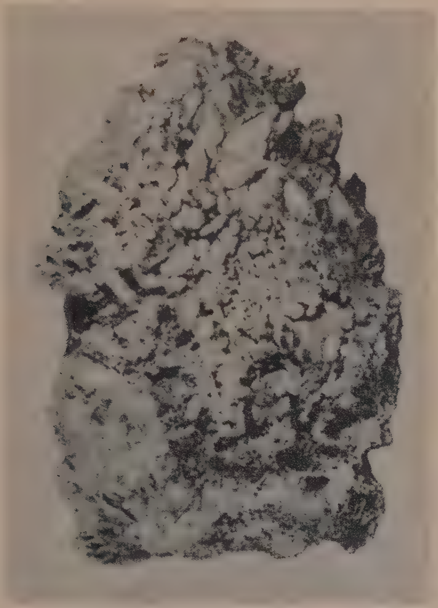

FIG. 3. Metacolloidal marcasite (botryoidal) from the Hobo mine. Slightly reduced.

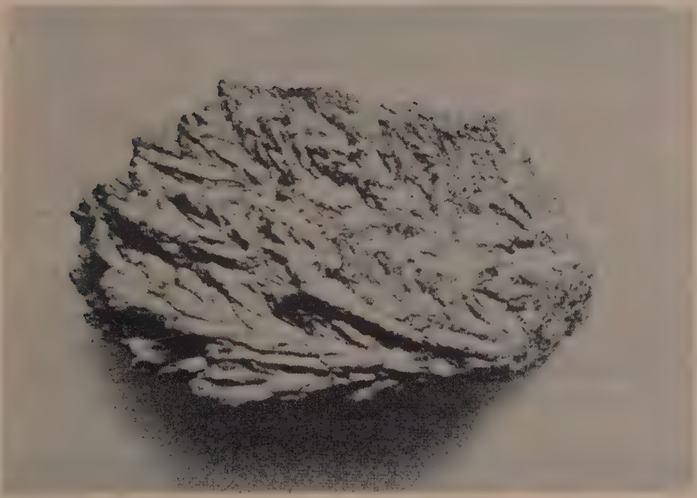

FIG. 4. Plumose marcasite from the Leslie mine. Slightly reduced.

their presence can be detected only by the sheen exhibited by reflected light. Not uncommonly, the fibrous metacolloid structures give way to dominantly finely granular marcasite containing barely sufficient fibers to support the aggregate. The plumose forms developed in the closing stages of deposition and contain many open spaces. Marcasite was not usually the last mineral to be deposited, but it may have been last.

The pyrite occurs primarily as drusy surfaces on the marcasite, as fibrous concentric bands or layers *alternating* with the marcasite, or as well developed crystals (normally 1–2 mm. across but, rarely, 2 cm.).

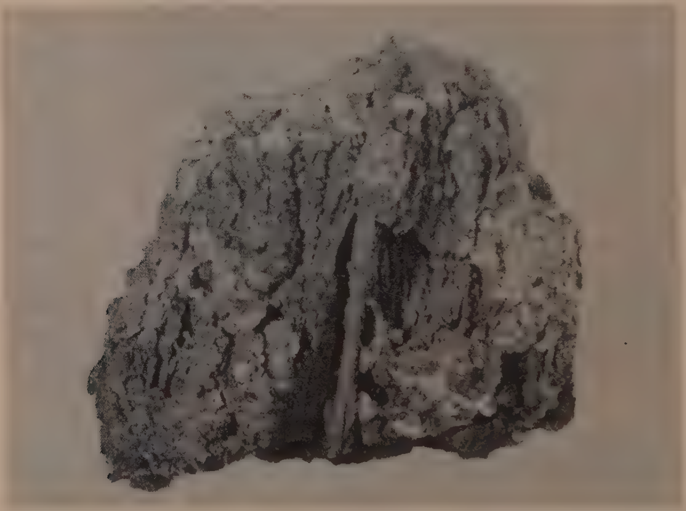

Fig. 5. Stalactitic marcasite. Moselle mine. Slightly reduced.

Some of the alternating bands are .05 millimeter or less in thickness, others may be one or two millimeters. Usually, the drusy layer is last and is a millimeter or less in thickness, but very rarely there may be a concentric layer of fibrous pyrite, two or three inches thick, terminating in crystals one inch across. Short (a few millimeters in length), lenticular (but concentric) layers of pyrite may occur within a fibrous radiating mass of marcasite.

The crystals of pyrite are usually cubes modified by octahedrons (less commonly by pyritohedrons) or octahedrons modified by cubes. A particular form or combination of forms usually dominates at each mine; thus pyritohedral forms on cubes are more common at the Ruepple and Moselle mines than elsewhere. Layers of cubes (modified by octohedrons) of pyrite occur in the Ruepple mine. Rarely, marcasite was deposited on pyrite as the last mineral, but the usual occurrence was pyrite last.

The quartz occurs as a clear transparent material filling interstices within the sulfides, or as crystals within the cavities. Rarely, it is amethystine or yellow, the latter, due to included limonite. The limonite was deposited with the first quartz on the walls of the cavities, and usually forms a colored layer about a millimeter thick. Transparent quartz followed if space was available. The quartz was deposited later than the sulfides and not uncommonly replaced them. This replacement usually occurred in the fibrous portions rich in granular marcasite, which was the first part to be replaced. The fibrous part was then replaced by quartz which was pseudomorphic after the marcasite, or, more rarely, enclosed it. If both marcasite and pyrite were present in alternating bands, the marcasite was replaced and the pyrite left to form alternate layers with the quartz. Later, the pyrite was leached out leaving the thin shells of quartz.

The sulfides were deposited in the open spaces (shafts or sink-holes) developed within the Gasconade or other formations, or they replaced any dolomite, chert, or sandstone therein. Both sulfides are found replacing the chert and sandstone, and it can scarcely be doubted that any dolomite present would have been replaced early in the mineralization. Residual masses of chert, sandstone, and clay occur within the ore, but no masses of dolomite. Possibly, all the dolomite had been removed during the development of the solution cavities.

The sulfide ore is soft and brecciated, and thus slumps and caves easily. This makes mining by underground methods very difficult and dangerous. Where possible, stripping is resorted to and the mining accomplished by open cut methods.

Alteration of Sulfides to Iron Oxides

The primary sulfides in the upper part of the sinks were converted into the iron ores by oxidation. This was accomplished after erosion (aided by elevation of the region) had brought the top of the sulfide ore bodies to the surface, establishing a variable portion of them above the ground-water level. Oxidizing solutions then penetrated this part of the ore body and converted the sulfides into hematite and limonite. Much of the resulting product was structureless, the alteration having reduced the sulfides to soft iron oxides. In local areas, however, masses of the iron oxides are pseudomorphic after the sulfides, preserving the details of the colloform and crystalline material. From specimens showing the successive stages of alteration, it is seen that the more easily altered marcasite (a condition furthered by greater porosity, especially of the granular aggregates) was the first to be attacked and converted into the iron oxides. Where the topographic position of the sulfide deposit prevented the rapid ingress of water with its oxygen, the alteration progressed slowly. Furthermore, the texture and composition (the relative amounts of the two sulfides) of the aggregates influenced the rate of oxidation. Slow alteration produced chiefly soft hematite, which, as far as can be determined from published descriptions, predominated in the iron ores.

The rapid alteration of a deposit produced much heat which induced significant changes in the alteration products. As the heat escaped upward through channels, or, more slowly, by conduction through the iron oxides, the oxides were dehydrated, and the temperatures were, locally at least, high enough (probably 250°–300°C.) to convert the red hematite into specularite (the "hard blue ore" of the earlier accounts of the mining of these deposits). At lower temperatures, the hematite became goethite. Locally, iron oxides in solution were deposited as beautiful crystals and rosettes of specularite in cavities in the ores. It is very probable that hot sulfur-bearing springs existed at the surface over these altering sulfide deposits.

Another important mineralogical change accompanied this heat development. The hot solutions took silica (from sandstone and chert) into solution and redeposited it in the surrounding sandstones (converting them into quartzites), or, carrying it down into the unaltered sulfides, deposited it as quartz (rock crystal, both limonitic and amethystine) in the openings of the sulfides, or as a replacement of them. These were not oxidizing solutions, as the sulfides remaining were unaltered. Near the top of the sulfide ore body, a little limonite from above was occasionally deposited *with* the quartz. The quartz is most abundant in the top of the sulfide ores and decreases rapidly downward, showing that it came from above. Later solutions (probably cool) deposited small amounts of dolomite, calcite, barite, and some rare minerals in the iron ores.

ORIGIN OF THE MARCASITE

It is believed that these marcasite ore bodies were deposited by magmatic waters within galleries and shafts previously formed by ground water below the ground-water level. The magmatic waters had their source in a telemagmatic batholith underlying the region. These solutions were acid and had a temperature of 100° to 125°C., which represents the optimum conditions for the deposition of marcasite. They probably transported the iron as the chloride. Hydrogen sulfide, also from the magma, entered the galleries and shafts and, where trapped in these openings, became sufficiently concentrated to react with the $FeCl_3$ to precipitate FeS_2. This marcasite or pyrite reaction was aided by the absence of much oxygen in these trapped solutions as the galleries and shafts were unconnected with the surface. The tops of the solution chambers were all below ground-water level at the time of the ore formation.

Possible reactions involved in the precipitation under the above conditions are as follows:

$$H_2S + 3O = SO_2 + H_2O.$$

Because there was insufficient oxygen to convert all the H_2S into SO_2, the SO_2 reacted with the H_2S to form free S:

$$2H_2S + SO_2 = 3S + 2H_2O.$$

In the presence of $FeCl_3$, conditions were then satisfactory to precipitate FeS_2, thus:

$$2FeCl_3 + 3H_2S + S = 2FeS_2 + 6HCl.$$

The HCl formed was used in dissolving the dolomite and some other substances, in this way facilitating replacement.

The following sequence presents briefly the writer's interpretation of the events involved in the origin of the sulfides, and in the alteration to iron oxides of that portion of the ore body occupying the upper part of the sinks.

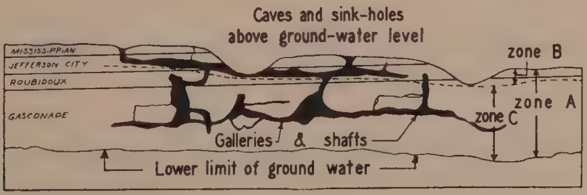

Fig. 6. Sketch to show the relationship of the various cavities to water level (dotted line).

1) Following the deposition of the Mississippian beds in the central Missouri area, the sea retreated, and post-Mississippian erosion subjected the region to peneplanation. The bottom of the ground-water zone was then (as at present) at variable depths below the surface. Within this zone (Fig. 6-*A*), the development of solution cavities was possible (and probable) both above (zone *B*) and below ground-water level.[3] As the formations involved were dolomites and sandstones, the

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[3] Davis, W. M., Origin of limestone caverns: *Bull. Geol. Soc. Am.*, vol. **41**, pp. 477–628, 1930.

lower ones of which (the Gasconade and Roubidoux) had been previously subjected to the attack of ground water and thus doubtless already contained solution cavities, it seems reasonable to assume that various types of solution cavities, galleries, and shafts were more or less fully developed below the water level (Fig. 6-*C*), as were caves and sink-holes also above it (Fig. 6-*B*). These openings were formed in the Mississippian (now removed from this area), Jefferson City (200 feet thick), Roubidoux, and Gasconade formations. It should be noted that the network of galleries and shafts of zone *C* were connected with the branch work of caves and sink-holes of zone *B*. At a late stage in the development of the peneplain, the water level was near the surface, hence the major solution work took place below this level, which favored the formation of many galleries and shafts.

2) In the area of the sulfide deposits, the Roubidoux and Gasconade formations were near or at the surface and were the seat of active solution work. Parts of these formations were evidently readily soluble as they contain numerous caverns today, many of which are believed to date to the pre-Pennsylvanian period of solution.[4]

3) Galleries formed wherever the top strata were strong enough to form a roof. Shafts developed where joints in the roof occurred, permitting vertical movements of the ground water (Fig. 7-*A*). The Gasconade is very cherty and the removal of the dolomite left the galleries partially filled with a brecciated mass of chert and clay but with ample space for circulation of the water.

4) The Pennsylvanian sea submerged the area, and sands and shales were spread over it, filling the sinks and sealing up the water in zone *A* (Fig. 6-*A*).

5) Following elevation at the close of the Paleozoic era, erosion was probably in progress throughout much if not all of the Mesozoic. Total erosion appears to have been small, as a thin sheet of Pennsylvanian beds is still present in nearby areas. This was probably due to the nearness of the land surface to sea level, and not improbably to submergence beneath Cretaceous seas although there is no proof of this. It is not believed that the Pennsylvanian formation was entirely removed from the area during Mesozoic time. The solution work of post-Mississippian times continued throughout the Mesozoic.

6) The sulfides were deposited by magmatic waters (in the manner shown above) during late Cretaceous time (Fig. 7-*B*), probably at much

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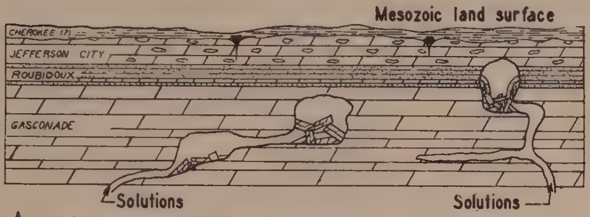
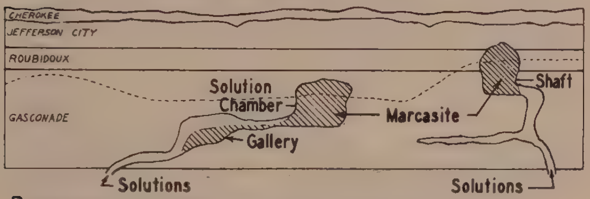
[4] Lee, Wallace, Geology of the Rolla Quadrangle: *Mo. Bur. Geol. and Mines*, vol. **12,** p. 70, 1913.

the same time as the occurrence of the mineralization in the Southeastern Missouri Lead district[5] and in the Arkansas and Tri-State areas.

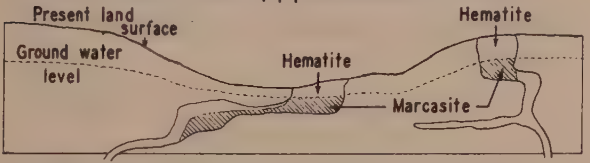
7) The H_2S and the magmatic waters rose from below and entered the galleries and shafts, the H_2S collecting in the highest parts of the gallery-shaft system (the present "filled sinks"), and thus being trapped under the Roubidoux, Jefferson City, or Pennsylvanian formations.



A-Solution cavities formed in post-Mississippian and early Mesozoic times



B-Deposition of the sulfide ore, probably in late Cretaceous time



C-Tertiary erosion and peneplanation, followed by uplift, exposed the sulfide ore-bodies, and the portion above water level was oxidized to hematite.

FIG. 7. Sketches to illustrate the sequence of events in the origin of the sulfide deposits.

8) Precipitation of marcasite (and pyrite) occurred in the open spaces in these traps, both sulfides being deposited as colloids (later becoming metacolloids) and crystalloids. Of the two, pyrite was more commonly deposited in crystalline form. The marcasite was deposited first from acid solutions, probably at about 100°C.,[6] and then, as the solution of

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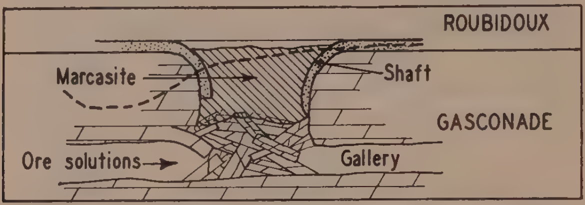
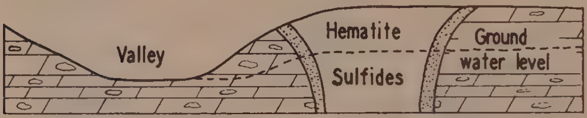
[5] Tarr, W. A., Origin of the southeastern Missouri lead deposits: *Econ. Geol.*, vol. **31**, pp. 712–754, 832–866, 1936.

[6] Allen, Crenshaw, and Johnston, The mineral sulphides of iron: *Am. Jour. Sci.*, 4th series, vol. **33**, p. 169–236, 1912.

the dolomite neutralized the waters, pyrite was deposited. This alternation of deposition of the two sulfides was repeated often as the solutions changed back and forth from acid to neutral or slightly acid, but always the amount of pyrite deposited was very subordinate. A similar alternation has been observed in a marcasite deposit in Madison County, Missouri.[7] The abundance of maracite and its universal colloform structure indicate predominant acid conditions and rapid deposition.



Ideal sketch of original conditions after deposition of the sulfides. Dashed line is the present land level.



The hematite was formed from the sulfides after the water level was lowered by the downward cutting of the valley.

FIG. 8. Sketch to show the origin of a sink-hole deposit of hematite and the sulfides.

9) Uplift at the close of the Mesozoic period reestablished the surface drainage and initiated a new period of peneplanation with its attendant ground-water system.

10) The near-surface water level of the Tertiary peneplanation period prevented oxidation of the sulfides, unless or until erosion exposed one of the shafts or gallery traps containing ore.

11) Late in the Tertiary period occurred the uplift that rejuvenated the Ozark streams which then vigorously entrenched themselves into the peneplain they had developed. The water level was thus lowered, and all the sulfide deposits above the level (the vadose zone) were vigorously attacked by oxidizing solutions (Figs. 7 *C* and 8). Marcasite is readily altered by oxygen and water, and the abundance of fine, granular (as

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[7] Tarr, W. A., Alternating deposition of pyrite, marcasite, and possibly melnikovite: *Am. Mineral.*, vol. **12**, pp. 417–421, 1927.

well as fibrous) marcasite in the very porous and brecciated (due to slumping) ore body intensified the oxidation which proceeded rapidly. The large amount of heat thus generated still further stimulated the reactions.

12) Parts of the resulting soft iron oxides above the zone of active alteration were changed by the hot gases and solutions to specularite (blue ore). The hot solutions, likewise, aided in removing silica, and where the circulation was favorable carried some of it down into the upper part of the unoxidized sulfides, depositing it as quartz in cavities or as replacement of marcasite.

13) That the oxidation of the marcasite deposits was related to this entrenchment and lowering of the water level is shown by the fact that the marcasite of the filled sinks is at about the level of nearby streams. In deposits on ridges where the water level is higher, the sulfides are higher than the adjacent streams (Fig. 8).

14) As grade was reached by the larger streams, down-cutting by all of them ceased; the water level became essentially stationary, and oxidation practically stopped, or it became so slow that all heat resulting from it was dissipated. Little change has occurred in either the iron ores or the remaining sulfides in recent geologic times, although the removal of the former within the last 50 or 75 years has exposed the latter to renewed (but slight) oxidation.

THE OCCURRENCE OF FINE GRAINED AUTHIGENIC FELDSPAR IN SHALES AND SILTS

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Introduction

The occurrence of secondary feldspar in sediments was reported as early as 1861 when Drian[1] and Lory[2] observed feldspar grains in limestones from the Alps. Since then secondary feldspar has been described by workers in different parts of the world and their findings have been reviewed by Boswell,[3] Twenhofel[4] and others. The more recent papers describing American occurrences are those by Daly,[5] Singewald,[6] Goldich[7] and Tester.[8] These investigators have demonstrated that small amounts of secondary feldspar are quite common and that they have a wide geologic and an equally wide geographic distribution.

Nearly all of the authigenic feldspar that has been described has been isolated from sandstones or from the insoluble residues of limestones and dolomites. In such rocks the observed grains vary from .008 mm. to 1.0 mm. in diameter. Many of the feldspar grains contain nuclear grains of detrital origin. For the present study the writers utilized x-rays to determine the composition of grains in shales and silts that are too fine-grained to be identified by their ordinary petrographic characteristics. It was found that orthoclase occurs in shales as grains less than a micron in diameter.

Materials and Methods Used

Samples from the Glenwood shale, the Decorah shale, and from shaley beds in the Oneota-Shakopee dolomites were studied and compared with clays and shales from other stratigraphic horizons. The Glenwood is a thin sandy and silty shale, the Decorah is somewhat calcareous and contains layers of dolomitic limestone. The Oneota-Shakopee dolomites constitute the Prairie du Chien group of the basal Ordovician. The accompanying section of the Glenwood as exposed in the wall of the Mississippi River Valley at Minneapolis, Minnesota, is typical of the formation. Petrographic analyses of its various phases have been published by the junior author.[9]

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[1] Drian, A., Notice sur les cristaux d'albite renfermes dans les calcaires magnesians des environs de Modane: *Soc. Geol. France, Bull.*, 2nd series, vol. **18,** p. 804, 1861.

[2] Lory, C., Comptes rendus d'une excursion geologique dans le Vallee d'Entremont (Savois); *Soc. Geol. France, Bull.*, 2nd series, vol. **18,** pp. 806–826, 1861.

[3] Boswell, P. G. H., *On the Mineralogy of Sedimentary Rocks.* T. Murby and Co., pp. 87–96, **1933.**

[4] Twenhofel, W. H., and others, *Treatise on Sedimentation*, 2nd Ed., pp. 591–596, **1932.**

[5] Daly, D. R., Low temperature formation of alkaline feldspars in limestones: *Proc. Nat. Acad. Sci.*, **III,** pp. 659–665, 1927.

[6] Singewald, J. T. Jr., and Milton, C., Authigenic feldspar in limestone at Glen Falls, New York: *Bull. Geol. Soc. Am.*, vol. **15,** pp. 463–468, 1929.

[7] Goldich, S. S., Authigenic feldspar in sandstones of southeastern Minnesota: *Jour. Sed. Petrol.*, vol. **4,** pp. 89–95, 1934.

[8] Tester, A. C., and Atwater, G. I., The occurrence of authigenic feldspar in sediments: *Jour. Sed. Petrol.*, vol. **4,** pp. 23–31, 1934.

SECTION OF THE GLENWOOD SHALE AT MINNEAPOLIS, MINN.

	Thickness in inches
1. Shale, calcareous	14
2. Shale, grayish green	4
3. Clay, soft, black, sticky	2
4. Shale, pale green, sandy	18
5. Sandstone, buff to white, clayey	20
6. Sandstone, ferruginous	12
7. Sandstone, ferruginous, banded	30
8. Sandstone, white	12
9. Sandstone, pale olive green	5

Outcrops of the Glenwood beds were sampled with special reference to layers with petrographic variations. In some instances an individual sample represented a layer no more than two or three inches in thickness. Beds numbered 4 and 5 of the Minneapolis section were studied most intensively.

TABLE 1

Diameter in mm.	Percent by Weight
1/2	2.28
1/4	8.44
1/8	2.67
1/16	48.81
1/32	5.96
1/64	0.34
1/128	2.26
1/256	3.69
1/512	25.02
less than 1/512	0.51
	99.98

In the procedure adopted a sample was disaggregated by placing it in a one per cent solution of sodium carbonate and agitating it in a soil dispersion machine. The shaking, combined with the peptizing effect of sodium carbonate produced a dispersed suspension. To remove all coarse detrital grains or aggregates the suspension was poured through a sieve with meshes of 1/16 mm. (.061 mm.). It was then placed in a graduated liter cylinder and fractioned into various size grades by differential settling. Krumbein's method[10] for the analysis of fine-grained sediments was employed. The accompanying textural analysis shows the size range ot the material in bed No. 4 (Table 1).

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[9] Thiel, G. A., A petrographic analysis of the Glenwood beds: *Bull. Geol. Soc. Am.*, vol. **48**, pp. 113–121, 1937.

The mechanical analysis shows two distinct maxima. One, between $\frac{1}{8}$ and 1/16 mm. grain size, comprises about 48% of the sample. Another between 1/256 and 1/512 mm. contains 25% of the total. The first is about 83% quartz. The second is mostly feldspar. It contains no quartz.

The fraction with grains 1/32 mm. in diameter and finer was analyzed chemically (Dr. R. B. Ellestad, analyst, Rock Analysis Laboratory, Univ. of Minn.). It contains

SiO_2	56.29
Al_2O_3	19.22
Fe_2O_3 (total iron)	4.39
Na_2O	.19
K_2O	10.85
H_2O-	3.54
H_2O+	2.04
TiO_2	.64
CaO	.09
MgO	1.65
SO_3	.72
	99.62

If all the K_2O is in the feldspar, 66% of the material is potash feldspar. The total water content is 5.58% of which 2.04% is lost at 110°C. This is almost completely regained if the sample is left standing in the laboratory for several days. The SiO_2 and Al_2O_3 not necessary for the feldspar are in the molecular ratio of about 3.2 to 1.0. This points to minerals of the montmorillonite-beidellite series. Their presence would account also for the MgO and for the fact that the material is capable of absorbing water from the atmosphere. Allophane could also be present.

The fractions 1/32 mm. in diameter and finer were x-rayed.* In eight separate fractions ranging from 1/32 to 1/5000 mm. only orthoclase lines appeared in the x-ray films. Neither quartz, mica, kaolinite, nor montmorillonite were present in sufficient quantities to be detected. It might be pointed out at this time that x-ray methods are not very sensitive for the detection of montmorillonite when in a mixture with feldspar. Its lines are so diffused (including the well known line near the zero beam) that it is very doubtful that an amount less than 15 per cent can be noticed at all.

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[10] Krumbein, W. C., The mechanical analysis of fine-grained sediments: *Jour. Sed. Petrol.*, vol. **2**, pp. 140–149, 1932.

* Unfiltered Fe radiation. Radius of camera 57.3 mm. Thickness of rods 0.7 mm.

Since the limits of the colloidal state have been generally accepted to lie between 0.1μ and 0.2μ diameter, the sediment finer than the last fraction obtained by the Krumbein method is mainly of colloidal size. This very fine material which constituted no more than a small fraction of one per cent of the sample was divided into two fractions. When x-rayed the coarser one showed feldspar and mica, whereas the finer showed only diffused mica lines. The particles in the finest fraction were probably smaller than 1/10 micron in diameter.

Samples of the Decorah shale were subjected to similar treatment. Some channel samples that represent a vertical interval of five feet, contain sufficient orthoclase to produce x-ray patterns in which the feldspar lines are most conspicuous although quartz and mica lines are also present. When fractioned by the pipette method it was found that orthoclase predominates in the fractions from 1/32 to 1/512 mm. The 1/1024 fraction gave only mica patterns when x-rayed.

The basal Decorah is represented by 8 feet of thin bedded dolomite. The insoluble residues derived from the dolomite were fractioned by the pipette method and x-rayed. The fractions from 1/32 mm. to 1/128 mm. and smaller were predominantly orthoclase. Some mica and quartz were present. The latter seems to be absent, however, in material below 1/128. Some shale beds in the Shakopee formation also are composed largely of feldspar. Numerous thin layers of sandstone and sandy shale are interbedded with dolomite along the valley of the Willow River near Burkhardt, Wisconsin. A sample of green shale taken below the dam one mile northeast of the village was first treated with HCl to eliminate the carbonates. Only 5 per cent was soluble. The insoluble residue was x-rayed without further separation. The orthoclase pattern was most conspicuous. Lesser amounts of quartz and mica were also present. The residue was then washed and allowed to settle for one minute. The material that remained in suspension was then x-rayed. It produced an orthoclase pattern only.

Samples of Cretaceous shale from southwestern Minnesota were also x-rayed. The quartz pattern was always predominant in them.

Origin of Fine-grained Feldspar

In contradistinction to detrital minerals which were formed by the disintegration of older formations, authigenic minerals are those that have been formed at the same time as or subsequently to the laying down of the sediment. The authigenic feldspar in the limestones and dolomites of Europe have long been considered of sedimentary origin. There has been a tendency to ascribe the growth of feldspar to the action of marine waters on argillaceous material in the calcareous ooze on the floor of the sea. Grandjean[11] concluded that in all the occurrences of feldspar recorded by him the mineral had grown relatively rapidly during slow sedimentation and that the crystals probably ceased to grow after burial of the sediment.

Tester and Atwater[12] have recently suggested that normal sedimentary processes of consolidation and cementation might also permit the growth of secondary feldspar. Their conclusions were based on a study of textural relations in thin sections of dolomitic rocks containing abundant authigenic feldspar.

Since much of the feldspar found in the silts and shales that were studied during this investigation is exceedingly fine-grained and remarkably free of other mineral grains one is not justified in postulating that it is of clastic origin. Fine-grained silts derived from the products of mechanical disintegration of igneous and metamorphic rocks are more or less siliceous. The Glenwood silt samples contain no quartz, however, in the fractions finer than 1/32 mm. Natural agents of sorting would scarcely separate quartz and feldspar of these dimensions, though clayey sediments of colloidal size may be sorted from finer silts. Another striking feature is the complete predominance of orthoclase. In detrital material plagioclase should be very common also. In view of the fact that much of the orthoclase is finer than 1/256 mm. it is hard to believe that it could have withstood the vicissitudes of weathering to which detrital material is subjected. It is much more likely that clayey material of colloidal dimensions and properties abstract potassium from solutions and form orthoclase under favorable conditions. Another alternative is to attribute the formation of the authigenic feldspar to hydrothermal activity.[13] A low-temperature form of orthoclase is known to occur in veins the temperature of formation of which is thought to be as low as 100°C. Increased temperatures due to deep burial of sediments might be sufficient therefore, to lead to the formation of feldspar. There is no evidence, however, that the early Paleozoic rocks overlapping on the pre-Cambrian shield in Minnesota have been buried to depths sufficiently great to raise their temperature appreciably. Furthermore, secondary feldspar has been reported from Cretaceous sandstones in Kansas, Nebraska and South Dakota where there is no evidence that either deep burial or volcanic emanations could have produced high temperatures for their formation.

[11] Grandjean, F. Propriétes optiques et genése du feldspath néogéne des sediments du bassin de Paris: *C. R. Acad. Sci., Paris*, vol. **148**, pp. 723–25, 1909.

[12] *Op. cit.*

[13] Gruner, J. W., Hydrothermal alteration of montmorillonite to feldspar at temperatures from 245°C. to 300°C.: *Am. Mineral.* vol. **21**, p. 515, 1936.

THE UNIT CELL AND SPACE GROUP OF STERNBERGITE, $AgFe_2S_3$

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Abstract

Sternbergite from Joachimsthal, Bohemia, has been studied by the equi-inclination Weissenberg method. It is evident from the results obtained in this work that the axial ratio derived by morphological study should be changed so that *b* has $\frac{1}{3}$ the length assigned to it by Peacock. This change also brings with it the necessity of interchanging the usual *a* and *b* axes in order to leave *b* the longer of the two.

The investigation leads to the following cell data, in terms of the new orientation:

Diffraction symbol: *mmmCc*− −
Crystal class: C_{2v} or D_{2h}
Crystal system: Orthorhombic
Space group: *Ccm* (C_{2v}^{12}) or *Ccmm* (D_{2h}^{17})
Unit cell:

Absolute	*Ratio*
$a=6.61$Å	0.568
$b=11.64$	1.
$c=12.67$	1.088

$Z=8$ $AgFe_2S_3$ per cell.

There is no real isomorphism between sternbergite and cubanite.

Introduction

Crystals of sternbergite from Joachimsthal, Bohemia, have recently been remeasured and redescribed by Peacock.[1] Through the courtesy of Professor Palache and Doctor Peacock, specimens of this material were obtained for *x*-ray diffraction study. One of the purposes of this investigation was to follow out Peacock's attempt at comparing sternbergite with cubanite.

Method

Because of the very soft and plastic nature of the mineral, crystals suitable for *x*-ray examination cannot be handled freely without deformation. An attempt was made to overcome this difficulty by working with the cluster while it was in direct contact with carbon dioxide ice. It is believed that this cooling helped to make the material more rigid and to reduce distortion during the detachment of the separate crystals.

Rotation photographs were taken for the three crystallographic axes, and Weissenberg resolutions were made of all the equators. In addition, equi-inclination resolutions were made for these three plane lattice stacking directions. These included the 1, 2, 3 and 4 levels about the *a* axis, the 1 and 2 levels about the *b* axis, and the 1, 2, 3, and 4 levels about the *c* axis. From these photographs the reciprocal lattice has been reconstructed in three different elevations.

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[1] Peacock, M. A., On the crystal form of sternbergite: *Am. Mineral.*, vol. **21**, pp. 103–108, 1936.

SYMMETRY

All the photographs exhibit the plane group symmetry C_{2l}. The centrosymmetrical crystal symmetry is therefore D_{2h}. Sternbergite is accordingly orthorhombic, and may belong to any of the three crystal classes D_2, C_{2v}, or D_{2h}, so far as the symmetry of the photographs alone is concerned.

THE UNIT CELL

Space Lattice Type

Each of the *c* axis *n*-level equi-inclination Weissenberg photographs exhibits a diamond pattern. The level stacking sequence in the *c* direction is 7.[2] The *a* and *b* axis *n*-level photographs display rectangular patterns, each having a level stacking sequence 10. The space lattice type is accordingly *C*-centered orthorhombic.

Lattice Constants

The cell constants obtained from the reconstructed reciprocal lattice, refined by measurements from the three equatorial photographs, are as follows:

N. W. Buerger		Peacock	Haidinger[3]
Absolute	Ratio*		
$a=11.64$Å.	1.761	.5913 (×3=1.7739)	.583 (×3=1.75)
$b=$ 6.61	1.	1.	1.
$c=12.67$	1.916	.6250 (×3=1.8750)	.838 (×2=1.676)

* It is likely that this ratio is more accurate than a ratio derived from goniometric measurements, since it is obtained from interatomic spacing measurements which are less sensitive to crystal deformation and distortion than the external surface angle measurements.

It is apparent from these values that the axial ratio derived by morphological study should be changed so that *b* has one-third the length

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[2] Buerger, M. J., The application of plane groups to the interpretation of Weissenberg photographs: *Zeits. Krist.*, vol. **91**, Fig. 26, p. 275, 1935.

[3] Haidinger, W., Description of sternbergite, a new mineral species: *Trans. Roy. Soc. Edinburgh*, vol. **11**, pt. I, 1828, pp. 1–7.

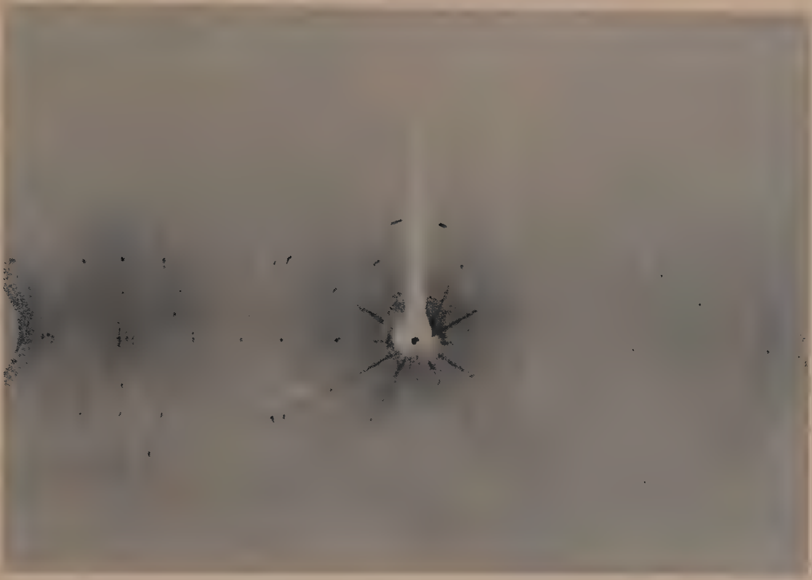


FIG. 1. Sternbergite, old *a* axis (new *b* axis) oscillation photograph.

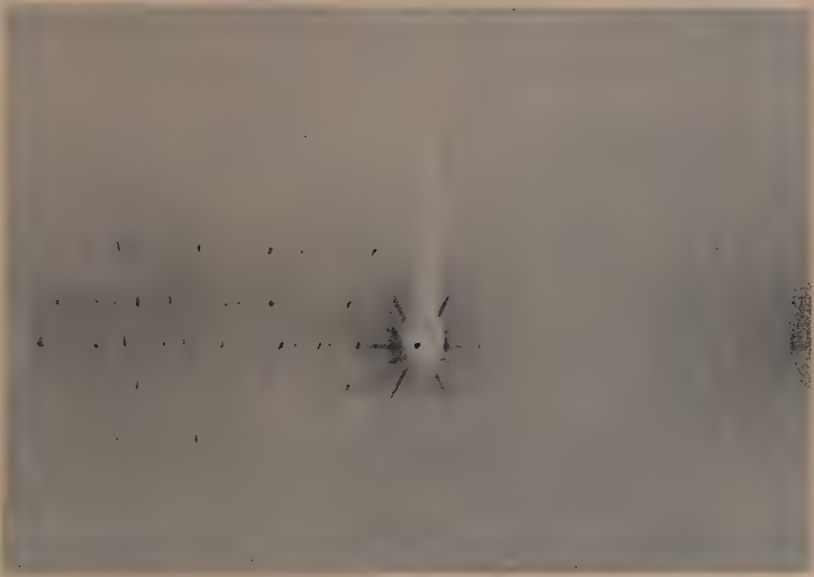
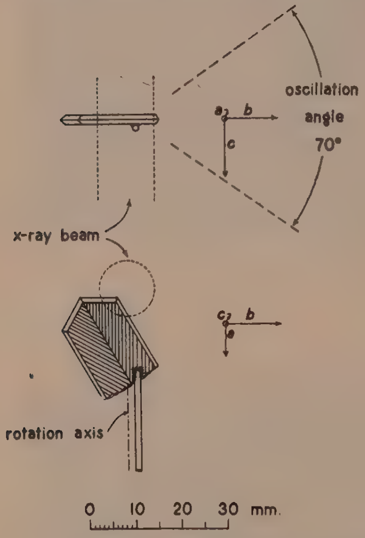


FIG. 2. Sternbergite, old *b* axis (new *a* axis) oscillation photograph.

assigned to it by Peacock. This change also necessitates the interchange of the *a* and *b* axial directions, in order to leave *b* the longer of the two. The need of changing the length of the *c* axis so that it has three times the length given it was foreseen by Peacock as a possible result of *x*-ray investigation.[4]

Since the proposed interchange of the *a* and *b* axes involves an important innovation in the accepted crystallography of sternbergite, photographic proof of the necessity of such an interchange is presented in Figs. 1 and 2. These are oscillation photographs about the old *a* and *b* axes, taken from portions of twins as shown in Figs. 3 and 4. A twin was used because twins are more resistant to deformation, and consequently provide cleaner photographs (less smeared spots) than untwined crystals. The crystal was oscillated about both the *a* and the *b* axes, through an angle of approximately 70°. The orientation was such that when the crystal was in the 35° position, the beam was normal to the crystal plate (parallel to the *c* axis); this allowed no portion of the other member of the twin to come within the path of the beam. The results, of course, are in harmony with the other rotation photographs. It is clear from Figs. 1 and 2 that the old reciprocal axis length, a^*, is less than the old reciprocal axis length, b^*; thus old *a* is greater than old *b*.



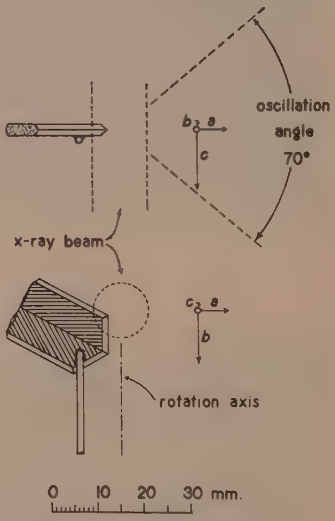


FIG. 3 (left). Method of obtaining old *a* axis (new *b* axis) oscillation photograph from individual of twin.

FIG. 4 (right). Method of obtaining old *b* axis (new *a* axis) oscillation photograph from individual of twin.

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[4] Peacock, M. A., *Op. cit.*, p. 104.

The new orientation results in the following cell constants:

Absolute	*Ratio*
$a=$ 6.61Å.	0.568
$b=$11.64	1.
$c=$12.67	1.088

The transformations of axes are shown in Table 1. It is of interest to mention here that Haidinger's notation of axes followed Mohs' old system in which the *a* axis was the principal, or vertical axis, *b* the macroaxis, and *c* the brachyaxis. Thus, Haidinger's *c* would be designated *a* in present day notation, and his *a* would be designated *c*.

The transformation of the form symbols is given in Table 2. It will be noted that with the new orientation, the forms are simplified in all cases

TABLE 1. TRANSFORMATION OF AXES

Haidinger	Peacock	N. W. Buerger
b →	b	
c →	a	
$\frac{3}{2}a$ →	c	
$3b$ →	→	a
c →	→	b
$\frac{3}{2}a$ →	→	c
	$3b$ →	a
	a →	b
	c →	c

TABLE 2. TRANSFORMATION OF FORMS

Haidinger to Peacock:* 300/030/002
Haidinger to Buerger: 010/300/002
Peacock to Buerger: 010/300/003

Haidinger	Peacock	N. W. Buerger
a (001)	*c* (001)	(001)
i (010)	*b* (010)	(100)
—(100)	*a* (100)	(010)
—(011)	*d* (032)	(102)
b (021)	—(031)	(101)
c (0·10·1)	—(0·15·1)	(501)
h (106)	—(104)	(014)
—(203)	*e* (101)	(011)
—(301)	—(902)	(092)
f (111)	*q* (332)	(132)
—(443)	*r* (221)	(263)
g (221)	*s* (331)	(131)
d (121)	—(362)	(232)
—(263)	*t* (131)	(111)
m (110)†	*m* (110)†	(130)†

* Transformation formulae according to Barker, *Systematic Crystallography*, p. 32, 1930.

† Twin plane only.

except Peacock's (221). A stereographic projection of the recorded forms of sternbergite, using the new orientation and axes, is given in Fig. 5.

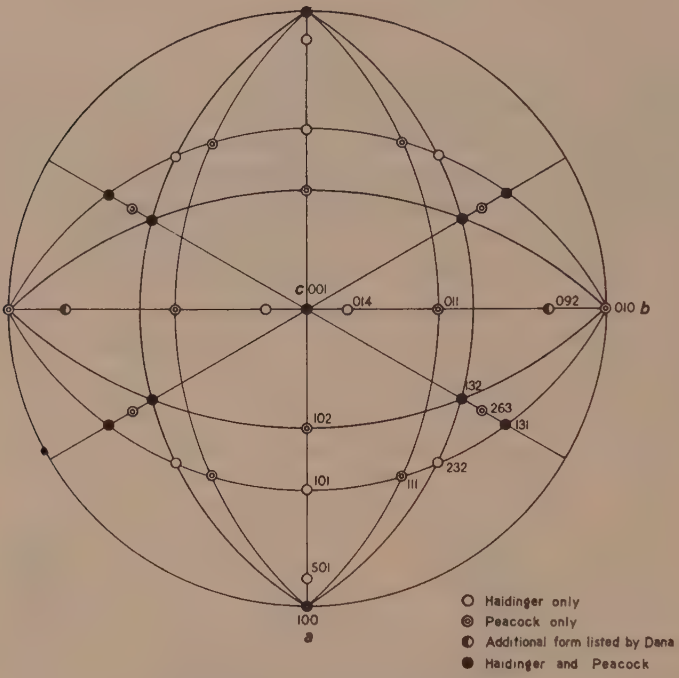

FIG. 5. Sternbergite. Stereographic projection of recorded forms, using new axes and orientation.

The cell contents may be calculated with the aid of the relation

$$\text{Measured density} = \frac{\text{cell mass}}{\text{cell volume}}$$

$$d = \frac{Z \times f \times 1.649 \times 10^{-24}}{V \times 10^{-24}}$$

where

d = measured density.
Z = number of formula weights per unit cell.
f = chemical formula weight.
V = cell volume in cubic Ångstroms.

Substituting the appropriate values of d, f, and V for sternbergite in this relation gives Z a value of $7.9 \approx 8$ formula weights per unit cell.

SPACE GROUP

Comparison of reciprocal cell translations on *n*-level and zero level equi-inclination Weissenberg photographs shows that in the (100) plane the *c* reciprocal translation is doubled, indicating a glide plane perpendicular to *a*, with glide component *c*/2. There are no other multiple reciprocal translations on the other zero levels. This total diffraction information may be expressed by the diffraction symbol *mmmCc*−−. The only possible space groups are therefore $Ccm(C_{2v}^{12})$ and $Ccmm(D_{2h}^{17})$. The symmetrical morphological development makes it probable that sternbergite is holohedral, which indicates D_{2h}^{17} as the probable space group. Figure 6 shows the space group in three projections.

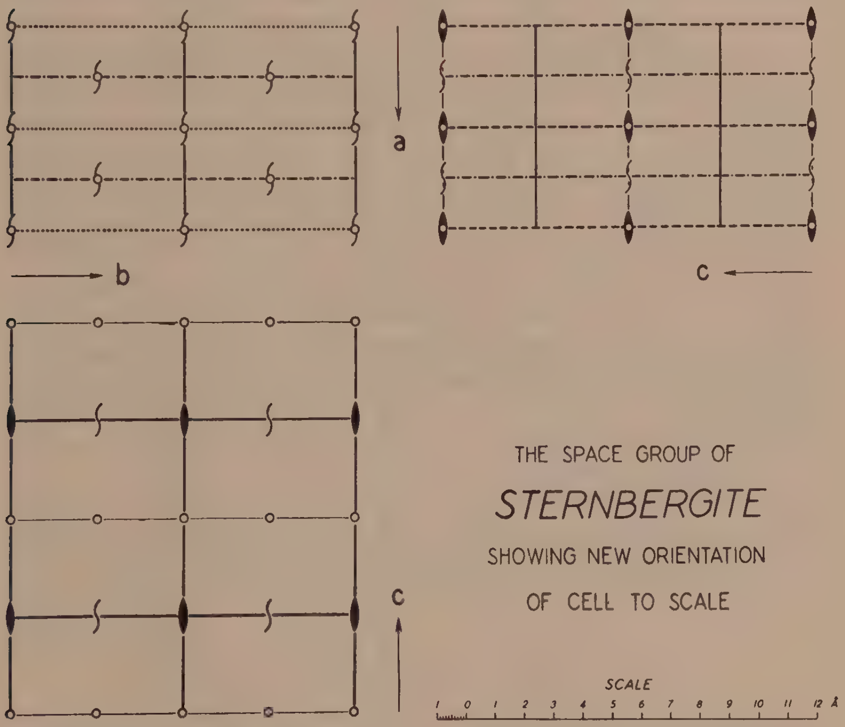

FIG. 6. The space group of sternbergite, showing new orientation to scale.

COMPARISON WITH CUBANITE

The lattice types and dimensions give no grounds for believing that any isostructural or isomorphous relation exists between sternbergite and cubanite, despite certain similarities displayed. Table 3 shows in tabular form a structural comparison between the two minerals. The *c* axis of sternbergite is about double that of cubanite. The two are certainly not strictly isostructural for sternbergite is based on a *C*– centered lattice (*C*) while cubanite is based on a simple lattice (*P*).

TABLE 3. STERNBERGITE CELL CONSTANTS (NEW ORIENTATION) COMPARED WITH CUBANITE CELL CONSTANTS

	Sternbergite	Cubanite*
absolute	$a=$ 6.61 Å.	6.43 Å.
	$b=$ 11.64	11.04
	$c=$ 12.67	6.19 (×2=12.38)
ratio	$a=$ .568	.582$_5$
	$b=$ 1.	1.
	$c=$ 1.088	.561 (×2= 1.122)
	$a/c=$ .521	1.038 (×$\frac{1}{2}$= .519)
lattice type	*C*	*P*
formula weights per cell	8 $AgFe_2S_3$	4 $CuFe_2S_3$

* Buerger, M. J., The crystal structure of cubanite: *Am. Mineral.*, vol. 21, p. 205, 1936.

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Professor M. J. Buerger for his valuable suggestions and help during the course of this investigation.

DENSITIES AND STRUCTURAL RELATIONSHIPS OF KAOLINITES AND ANAUXITES

John W. Gruner, *University of Minnesota, Minneapolis, Minnesota.*

Introduction

When the writer proposed the crystal structure of kaolinite in 1932[1] he also suggested the same structure for anauxite. Due to the higher $SiO_2:Al_2O_3$ ratio of anauxite it would be necessary, however, for Si ions to occupy some of the Al positions. It was expected that this proposal would not go unchallenged. The first to question it was Machatschki[2] who in his review of the writer's paper suggested that there were vacancies with four coordinates in the structure where additional Si could be placed. He did not indicate these positions. Ksanda and Barth[3] were able to secure some single crystals of dickite and obtained some *x*-ray reflections which had not been observed in powder photographs. Some doubt was therefore cast on the correctness of the structure of dickite as proposed by the writer.[4] Since its structure is very similar to that of kaolinite it could not fail to raise doubts as to the acceptability of the structure of the latter. Quite lately, however, Hendricks has shown that the writer's structure of kaolinite is correct.[5] He also came to the conclusion that anauxite has essentially the same structure as kaolinite. According to him the increase in the $SiO_2:Al_2O_3$ ratio is brought about by a subtraction of Al ions from the structure instead of by substitution of Si for Al. This would leave "holes" in the structure, of course. In order to investigate this suggestion further the writer obtained as many purified and analyzed samples of anauxite and kaolinite as possible of the material described in detail by Ross and Kerr.[6] He is greatly indebted to them and Dr. W. F. Foshag for these specimens, and to Messrs. Ernest Berg and Lynn Gardiner for assistance in the laboratory. Grants from the Graduate School of the University of Minnesota made this study possible.

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[1] Gruner, J. W., *Zeits. Krist.*, vol., **83**, pp. 75–88, 1932.

[2] *Neues Jahrb.*, *Referate* **I**, p. 439, 1933.

[3] Ksanda, C. J., and Barth, T. F. W., *Am. Mineral.*, vol. **20**, pp. 631–637, 1935.

[4] Gruner, J. W., The crystal structure of dickite: *Zeits. Krist.*, vol. **83**, pp. 394–404, 1932. According to a written communication received from Dr. S. B. Hendricks, the space group of dickite is C_s^4 as proposed by me. The arrangement of the ions in individual layers may be somewhat different, however, from that proposed by the present writer.

[5] Hendricks, Sterling B., Concerning the crystal structure of kaolinite, $Al_2O_3 \cdot 2SiO_2$ $2H_2O$, and the composition of anauxite: *Zeits. Krist.*, vol. **95**, pp. 247–252, 1936.

[6] Ross, C. S., and Kerr, P. F., The kaolin minerals: *U. S. Geol. Survey, Prof. Paper* **165-E**, pp. 161–165, 1931.

Density Measurements

The removal of Al^{3+} and of corresponding amounts of OH^- or O^{2-} from the structure should decrease the density of kaolinite. Reliable density measurements on analyzed samples of kaolinite and anauxite are scarce. The two factors which influence the trustworthiness of published observations most are, of course, the impurities and the grain sizes of the specimens. It was fortunate, therefore, that the writer had at his disposal seven actually analyzed and optically described samples. The following specimens were used:

No. 2, Anauxite from Bilin, Czechoslovakia.
No. 3, Anauxite from Mokelumne River, Lancha Plana, Calif.
No. 4, Anauxite from Newman Pit, Ione, Calif.
No. 7, Kaolinite from Roseland, Va.
No. 8, 9, Kaolinite from 1 mile south of Ione, Calif.
No. 10, Kaolinite from Abatik River, Northern Alaska.
"Newton Creek" from Subway tunnel, Brooklyn, N. Y.

The first six numbered specimens are described in detail in Ross's and Kerr's paper.[7] The "Newton Creek" kaolinite was described by Kerr in 1930[8] and was the specimen used in the writer's structural analysis[9] of kaolinite. Three of the specimens, namely Nos. 4, 8–9, and "Newton Creek" were available in sufficiently large quantities to make possible measurements with a silica glass pycnometer (10 cc.). Of the others the writer had only small amounts for determinations of the densities with heavy liquids. The pycnometer fluid used was tetrahydronaphthalene which is especially recommended for exceedingly fine-grained material since it wets the grains more thoroughly than does water. The density of the liquid was calculated from the known volume of the silica glass pycnometer and the weight of the liquid in it. Observations were also made with the Westphal balance. Great care was exercised in the removal of air bubbles. The mineral covered with fluid was shaken and stirred with a platinum wire occasionally during a period of four hours before the weighings were made.

Determinations were also made by centrifuging in heavy liquids. Bromoform diluted with alcohol was used at first. It was found, however, that alcohol was selectively adsorbed and all readings were much lower than when the bromoform was diluted with carbon tetrachloride. As a precaution against coagulation of the mineral powders the samples were shaken in the liquids of approximately the same density for an hour before they were centrifuged. It is obvious that there existed a slight range in the densities of different particles in the same sample. Therefore, no readings of the specific gravity were made at the very beginning of the sinking of the particles, neither after all the powdered material had settled. Readings with the Westphal balance were taken *before the bulk* of the sample had sunk and *after the bulk* of the sample had reached the bottom of the container. These two were averaged and constitute one determination in Table 1. All the observations are recalculated to 4°C. All samples (except No. 7 which was accidentally lost after centrifuging) were *x*-rayed. The dimensions of their unit cells (Table 1) are directly comparable with one another as they were run in the same camera. Unfiltered Fe radiation was used. Radius 57.3 mm. Diameter of specimens 0.6 to 0.7 mm.

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[7] *Op. cit.*

[8] Kerr, P. F., *Am. Mineral.*, vol. 15, pp. 153–154, 1930.

[9] *Op. cit.*

Table 1. Densities and Dimensions of Unit Cells of Anauxite and Kaolinite

No.	Ratio SiO_2: Al_2O_3	Density			Theor.* Density	Unit Cell Dimensions[9]			
		Cited in literature	Calculated to 4°C.			d_{001}	b_0	a_0	Vol. Å^3
			Pycnometer	Centrifuge					
2	274:100	2.524[1] 2.525		2.530[6]	2.581	14.27	8.95	5.17	660
3	267:100			2.510[7]	2.589	14.28	8.93	5.16	658
4	230:100		2.607[3]	2.579[8]	2.601	14.26	8.92	5.15	655
"N.Cr."	201:100		2.581[5]	2.588	2.589	14.28	8.93	5.16	658
7	197:100			2.538					
8, 9	195:100	2.585[2]	2.581[4]	2.572[8]	2.589	14.27	8.93	5.16	658
10	189:100			2.604	2.593	14.25	8.93	5.16	657

* Assuming theoretically pure kaolinite.

[1] Dittler and Hibsch, *Op. cit.*, p. 87. No method mentioned.

[2] Ross and Kerr, *Op. cit.*, p. 165. No method mentioned.

[3] Contained some grains of quartz. Size of sample 3.2 g.

[4] Hand picked but unground material. Size of sample 2.5 g.

[5] Exceedingly fine-grained. Size of sample 1.5 g.

[6] Average of 5 determinations.

[7] Average of 4 determinations.

[8] Average of 3 determinations.

[9] ±0.01 Å for b_0 and a_0, ±0.02 Å for d_{001}.

Discussion of Results

Hendricks,[10] in discussing the writer's proposal, shows by plotting the results of actual analyses that the H_2O content does not decrease quite as rapidly in anauxite as would be expected. He does not include in his calculations any H_2O driven off below 110°C. Though this is a commonly accepted procedure to get rid of "adsorbed" water, it is questionable whether it leads to comparable results in kaolinites. One needs to inspect only the numerous analyses of anauxite from Bilin, Bohemia,[11] to conclude that the H_2O ratio can be used only in a very general way as an indicator of structural differences between anauxite and kaolinite. This is also brought out graphically in Fig. 1.

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[10] *Op. cit.*

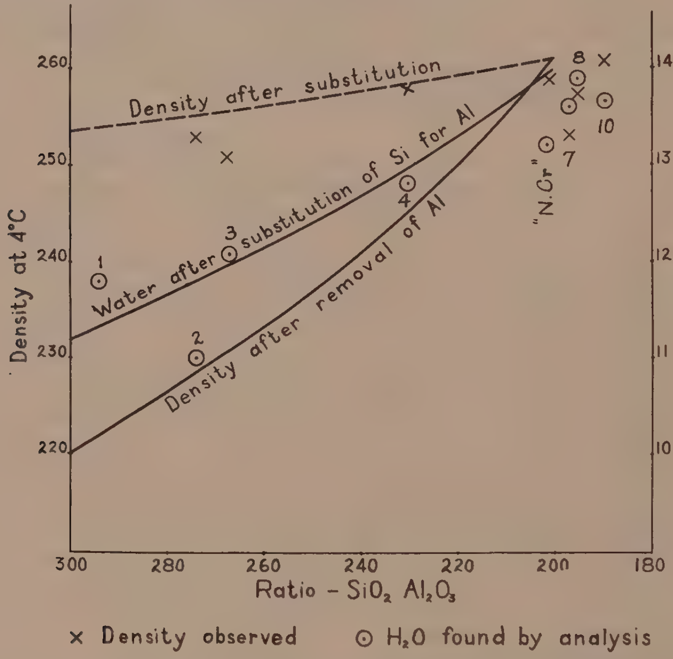

FIG. 1. Curves showing theoretical densities after removal of Al and on substitution of Si for Al respectively. Curve showing H_2O content on substitution of Si for Al and observed H_2O.

Densities should offer a much more reliable clue. For example, it would be possible though unlikely to place an SiO_4 group in the hexagonal ring shown in Fig. 2, a position to which Machatschki probably referred.[12] The density would be materially increased, however, and a very large part of the H_2O would be lost, obviously a condition not substantiated by the facts. Then there is Hendricks' proposal of taking

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[11] Ross and Kerr, *Op. cit.*, p. 163, and Dittler, E., and Hibsch, J. E., *Tschermak's Min. Mitt.*, vol. **36**, p. 87, 1925.

[12] *Op. cit.*

Al^{3+} ions out of the structure and for every Al^{3+} lost of removing two OH$^-$ and changing one O^{2-} to OH$^-$. Under these conditions the theoretical densities would not agree with observations. In Fig. 1 the writer has plotted the curve on which the densities should lie and the actual points as measured with heavy liquids. While it is true that two of the three anauxites are somewhat lower than the kaolinites they are far from the curve on which they would be expected.

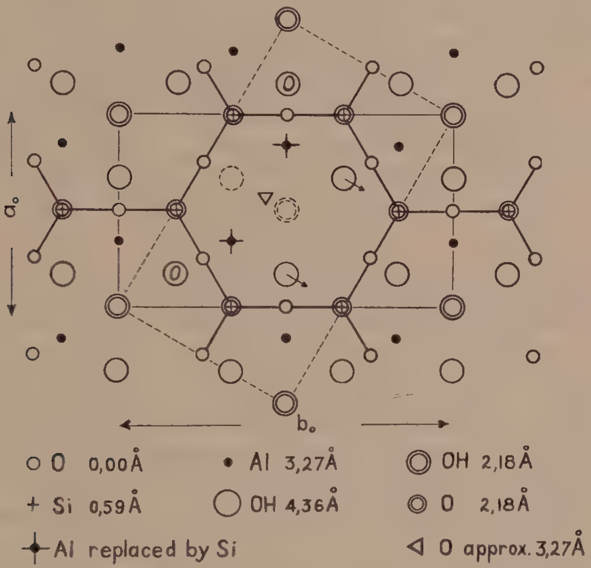

FIG. 2. Ionic positions in a single sheet of kaolinite and proposed changes in anauxite. The numbers indicate the heights of ions above the plane of projection.

The writer believes, therefore, that while his original proposal of placing Si ions in the positions of Al ions may have been too drastic, it is probable that whole units of tetrahedral SiO_4 occupy positions of octahedral units of $AlO_2(OH)_4$. The substitution may be explained with the aid of Fig. 2 which is a modification of one in the original paper[13] on kaolinite. For every pair of Si^{4+} substituted for two Al^{3+} (large crosses) two OH$^-$ are lost (dotted circles) and two OH$^-$ are converted to O^{2-} (large circles containing the letter O). A new O^{2-} (small triangle) occupies a position between the new Si ions. The two OH$^-$ groups designated by small arrows move slightly in the direction indicated. The structure is balanced, of course. But there must be some distortion of the octahedral groups and probably a slight one of the SiO_4 groups. The substitution will occur in pairs of SiO_4 groups which makes the retention of the original symmetry C_s^4 possible. If this were not the case it should be visible in a displacement of the lines in the powder photograph. Instead only a few slight differences in intensities are noticeable.

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[13] *Op. cit.*

It may be thought that the H_2O content of anauxite should be much lower if the writer's proposal be correct. Inspection shows, however, that even with a ratio $SiO_2:Al_2O_3=300:200$ only 0.8 Al has been replaced by Si in each unit cell and the theoretical H_2O has decreased from 13.96 to only 11.17 per cent. The curve showing the theoretical percentages of H_2O remaining in the structures is plotted in Fig. 1. It is seen that the writer's proposed change agrees about as well with the analyses as that of Hendricks as far as loss of water is concerned. The theoretical densities decrease so gradually that their curve (dotted line Fig. 1) shows a gentle slope.

CONCLUSIONS

The problem of the differences in the structures of kaolinite and anauxite has been discussed lately by Hendricks who concludes that the higher $SiO_2:Al_2O_3$ ratio in anauxite is due to removal of Al^{3+} and OH^- leaving a defect structure with holes. Density observations on seven analyzed samples of anauxite and kaolinite do not seem to agree with this suggestion. While anauxite seems to be slightly lower in density in two out of three cases it is not very likely that the deficiency of Al can be explained satisfactorily in this manner. The writer proposes a substitution of tetrahedral SiO_4 groups for octahedral $AlO_2(OH)_4$ groups. The loss of OH caused by this exchange is in as close agreement with analyses as can be expected. The method of density measurements by centrifuging in heavy liquids seems to give as accurate results as the use of the pycnometer if certain precautions are observed.

THE CRYSTAL STRUCTURE OF PLAZOLITE

Adolf Pabst, *University of California, Berkeley, California.*

Plazolite was described by Foshag[1] from the metamorphosed limestone at Crestmore, Riverside County, California, and as far as the writer is aware has not been reported from other localities. It is found in small colorless dodecahedrons superficially resembling grossularite but with a density of 3.129 and an index of refraction of 1.675. Foshag assigned to plazolite the formula $3CaO \cdot Al_2O_3 \cdot 2(SiO_2, CO_2) \cdot 2H_2O$ and stated that it seems to be most nearly related to sodalite. Winchell[2] suggested that it is closely related to ugrandite garnet.

Through the courtesy of Dr. E. P. Henderson of the United States National Museum the writer obtained a few small crystals of plazolite and a rock fragment from which other minute crystals could be separated. Through the kindness of Mr. W. H. Dore of the Division of Plant Nutrition of the University of California, Berkeley, it was possible to obtain excellent diffraction patterns from crystals and powder of plazolite.

All powder patterns were obtained in a cassette of 8 inch radius with molybdenum radiation screened by zirconium oxide. The cassette radius was checked by a calcite pattern or the film corrected by comparison with a halite pattern on the same film. The effective wave length of the unresolved molybdenum K_α radiation was in all cases taken to be 0.710Å.

In Table 1 are given the measurements of a plazolite powder pattern. From this the length of the edge of the unit cube is found to be 12.14 ±0.01Å, later checked by a rotation pattern.

Using Foshag's value for the density, 3.129, and a ratio of SiO_2 to CO_2 of 8.1, the average from Foshag's analyses, the number of "molecules" in the unit cube is found to be 8.032. Assuming 8 "molecules" in the unit cube the density would be 3.116. Again using the density 3.129 but assuming the composition to be $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which agrees fairly well with Foshag's analysis III, the unit cube would contain 7.966 "molecules." With just 8 of these "molecules" in the unit cube the density would be 3.141.

Since both results show fair agreement of composition, density and lattice constant the CO_2 content will hereafter be disregarded and the formula just given used in all later calculations.

All lines in the powder pattern have $h+k+l=2n$, showing that plazolite has a body-centered lattice and none of the space groups based on such a lattice are excluded by the powder data. Laue patterns taken with unscreened molybdenum radiation, a plate to crystal distance of 5 cms., with the incident ray parallel to [110] and to [001] showed the Laue symmetry O_h. This still leaves T_d^3, T_d^6 O^5, O^8, O_h^9 and O_h^{10} as possible space groups.

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[1] Foshag, W. F., Plazolite, a new mineral: *Am. Mineral.*, vol. **5**, pp. 183–185, 1920.

[2] Winchell, A. N., *Elements of Optical Mineralogy*, part **II**, 3rd edition, page 183, New York, 1933.

Table 1. Powder Pattern of Plazolite

2θ	$\sin^2\theta=(h^2+k^2+l^2)q.$	hkl
8.20°	6×0.000853	211
12.54	14×0.000853	321
13.45	16×0.000857	4(100)
15.03	20×0.000855	2(210)
15.73	22×0.000851	332
16.46	24×0.000854	2(211)
17.17	26×0.000857	431
18.44	30×0.000856	521
19.03	32×0.000855	4(110)
20.75	38×0.000853	611, 532
21.29	40×0.000853	2(310)
23.43	48×0.000858	4(111)
24.36	52×0.000856	2(320)
25.32	56×0.000858	2(321)
27.04	64×0.000855	8(100)
30.34	80×0.000856	4(210)
31.13	84×0.000857	2(421)
31.92	88×0.000859	2(332)
33.66	98×0.000855	941, 853
34.71	104×0.000855	2(510, 2(431)
35.75	110×0.000856	10.3.1, 952, 765
36.72	116×0.000855	2(520), 2(432)
37.39	120×0.000856	2(521)
38.57	128×0.000852	8(110)
40.95	144×0.000850	12(100), 4(221)
41.31	146×0.000852	12.1.1, 11.4.3, 981, 974
42.21	152×0.000853	2(611), 2(532)
44.18	164×0.000852	2(621), 2(540), 2(443)
46.18	180×0.000854	2(630), 2(542)
	average value of $q=0.000855$.	

With 8 "molecules" in the unit cube it is necessary to accommodate

24 Ca,
16 Al,
16 Si,

$$\left.\begin{array}{r}96\ \text{O}\\ \text{and }32\ \text{H}\end{array}\right\}\text{or 96 (O and OH).}$$

This cell content is somewhat similar to that of garnet for which a structure has been found in the space group O_h^{10} by Menzer.[3]

The plazolite powder pattern closely resembles garnet patterns. For better comparison powder and rotation patterns were prepared from grossularite, the garnet nearest to plazolite in composition. The grossularite used was analyzed material from near Georgetown,[4] California. The lattice constant determined from 24 lines on an excellent film corrected with halite is 11.85±0.01Å, close to the value, 11.840±0.003Å,

TABLE 2. COMPARISON OF INTENSITIES IN POWDER PATTERNS OF PLAZOLITE AND GROSSULARITE

Plazolite	*hkl*	Grossularite	
		observed	calculated
w	211	—	0.00
w	321	—	0.07
s	4(100)	s	1.02
vs	2(210)	vs	3.05
vw	332	w	0.26
m	2(211)	m	0.79
m	431	m	0.43
s	521	m	0.53
vw	4(110)	w	0.13
s	611, 532	s	0.79
vw	2(310)	—	0.00
w-m	4(111)	m	0.49
s	2(320)	s	1.16
vs	2(321)	vs	
w-m	8(100)	w-m	
—	741	vw	
m	4(210)	m	
w	2(421)	m	
w	2(332)	w	
vw	941, 853	w	
vw	2(510), 2(431)	vw	
vw	10.3.1, 952, 765	vw	
w	2(520), 2(432)	m	
w	2(521)	w	
w	8(110)	w	
vw	12(100), 4(221)	w	

vs=very strong, s=strong, m=medium, w=weak, vw=very weak.

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[3] Menzer, G. Die Kristallstruktur der Granate, *Zeits. Krist.*, vol. **69**, pp. 300–396, 1928.

[4] Pabst, A., Vesuvianite from Georgetown, California: *Am. Mineral.*, vol. **21**, pp. 1–10, 1936.

given by Menzer. The density was redetermined by suspension in a solution of thallium formate to be 3.55, whereas the density calculated from the lattice constant is 3.60.

Table 2 shows the similarity of the plazolite and grossularite powder patterns and the good agreement of the observed intensities of the grossularite lines with the intensities recalculated from the structure found by Menzer. The calculations were made by the usual formula, $I_{hkl}=j\cdot F^2\cdot(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$, using James and Brindley's values for the scattering powers of the ions. This gives an even better agreement of observed and calculated intensities than Menzer's method of calculation in which he assumed the scattering power to be proportional to the squares of the atomic numbers.

The two films show a close similarity. The most conspicuous differences are the appearance of the weak lines 211 and 321 in plazolite, the decrease of intensity of 332 and the increase of intensity of 611 and 532 in the plazolite pattern. The differences are also discernible in the photometer curves of the powder patterns, kindly prepared by Professor F. A. Jenkins of the Physics Department, shown in Fig. 1.

Rotation patterns of both plazolite and grossularite were prepared using unscreened molybdenum radiation, a planar film and a film to crystal distance of 5 cms. For the plazolite patterns it was necessary to use a crystal only 0.2 mm. on edge but even this was finally adjusted and both patterns showed a great number of spots that could be indexed with certainty. From Table 3 it may be seen that the differences in the two rotation patterns are essentially the same as those found by comparison of the powder patterns.

The structure of grossularite found by Menzer has 8 "molecules" in the unit cube. The lattice is body-centered and the space group is O_h^{10}. From this it seems that the structure of plazolite must be much like that of grossularite.

The atomic positions for grossularite given by Menzer are:—

16 Al in 16(*a*) 000;
24 Ca in 24(*c*) $\frac{1}{4}\,\frac{1}{8}0$;
24 Si in 24(*d*) $\frac{1}{4}\,\frac{3}{8}0$;
96 O in 96(*h*) xyz,

where x, y and z are 0.04, 0.055 and 0.64. From one film Menzer obtained the values, 0.035, 0.055 and 0.65, for x, y and z.

In the unit cube of plazolite it is necessary to accommodate

16 Al,
24 Ca,
16 Si
and 96 O and OH.

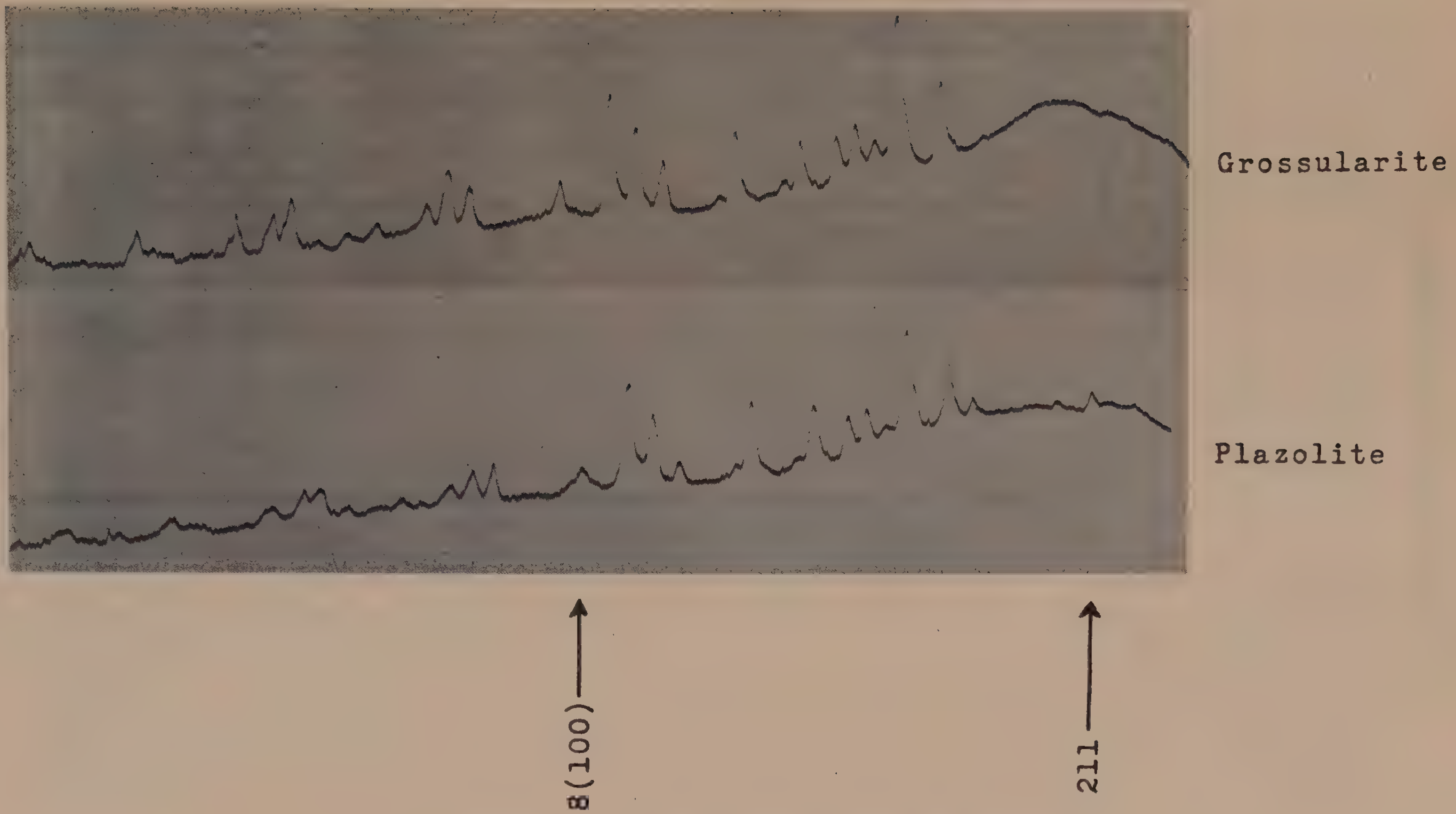

FIG. 1. Photometer curves of powder patterns of plazolite and grossularite.

TABLE 3. COMPARISON OF ROTATION PATTERNS OF PLAZOLITE AND GROSSULARITE

Layer Line																
Zero	400	420	440	620	640	800	840	10.4.0	880	12.0.0	12.6.0	14.4.0				
P	s	vs	vw	w	s	s	m	w	w							
G	s	vs	vw	vw	s	m	m	w	w	vw	vw	vw				
First	211	321	431	521	611											
P	w	vw	w	m	s											
G		?	w	w	m											
Second	112	312	042	422	512	532	642	842	10.4.2	12.2.2	12.8.2					
P	vw	w	vs	m	m	w	s	w	w	vw						
G			s	m	w	vw	m	m	w	w	w					
Third	213	323	413	523												
P		w	m	m												
G		w	w	w												
Fourth	024	224	314	044	444	064	264	084	284	664	864, 10.0.4	10.2.4	10.6.4	12.4.4	10.8.4	10.10.4
P	vs	m	m	vw	m	m	s	w	w	vw	w	vw	vw		vw	
G	vs	m	m	vw	s	m	s	w	m	w	w	w		vw	vw	vw
Fifth	215	325	525													
P	s	m	w													
G	m	w														
Sixth	116	026	046	246	516	646	846	10.4.6	12.0.6	12.6.6						
P	s		s	s	vw	w	vw	vw								
G	s	w	s	s		m	m	vw	vw	vw						
Eighth	048	248	468	088	488	10.4.8	888									
P	m	m	w	m	vw											
G	m	m	w	m	vw	vw	vw									
Tenth	0.4.10	2.4.10	4.6.10	4.8.10												
P	w	w	vw													
G	w	m	vw	vw												

The space group O_h^{10} has two 16-fold positions with the symmetry C_{3i} and D_3 respectively, which would not allow the placing of Si in either of these positions if it is to be at the center of an SiO_4 tetrahedron. Since this rules out 16-fold positions for Si in this space group the only remaining possibility is that the Si ions are either in a shared or in a partly vacant set of positions.

Table 4. Comparison of Calculated and Observed Intensities in a Powder Pattern of Plazolite

hkl		Calculated intensities			Observed intensities
	x	0.04	0.035	0.035	
	y	0.055	0.055	0.04	
	z	0.64	0.65	0.65	
211		0.03	0.30	0.11	w
2(110)		0.11	0.00	0.03	—
321		0.26	0.17	0.12	w
4(100)			0.81	1.22	s
2(210)			2.20	2.69	vs
332			0.27	0.09	vw
2(211)			0.60	0.38	m
431				0.50	m
521				0.70	s
4(110)				0.10	vw
532, 611				0.50, 0.57	s
2(310)				0.10	vw
541, 631				0.00	—
4(111)				0.54	m
543				0.07	—
2(320)				0.78	s
633, 255,* 217				0.02, 0.05, 0.00	—
2(321)				1.48	vs
651, 732†				0.07, 0.00	—
8(100)				0.51	m

* Not discernible on powder pattern, but 255 appears in fifth layer line of rotation pattern.

† This line not measured on powder pattern though discernible on photometer curve and 516 appears in rotation pattern.

The simplest assumption that suggests itself is that the arrangement of ions in plazolite is similar to that found by Menzer for grossularite but with only 16 Si distributed at random in 24(*d*).

Calculation of the intensities of lines in the powder pattern showed fair agreement but did not fully account for the differences in the plazolite and grossularite patterns. Further trial intensity calculations were then made with various sets of oxygen parameters, assigning to OH^- the same scattering power as to O^{-2}. Good agreement was obtained with the parameters 0.035, 0.04 and 0.65. Table 4 shows the agreement of calculated intensities of all lines with $h^2+k^2+l^2 \leqq 64$ that may appear in space group O_h^{10} with the observed intensities.

This table also shows a few calculated intensities for plazolite with the two sets of oxygen parameters in grossularite given by Menzer. In each case the calculations were carried only far enough to eliminate a given set of parameters and in this way half a dozen other sets besides those given in the table were eliminated.

TABLE 5. SILICON-OXYGEN DISTANCES IN PLAZOLITE FOR VARIOUS OXYGEN PARAMETERS

Oxygen	x	y	z	x	y	z	x	y	z
Parameters	0.04	0.055	0.64	0.035	0.055	0.65	0.035	0.04	0.65
Si-O Distance	1.80Å			1.75Å			1.704Å		

Table 5 shows the distances from O to Si in plazolite with the three sets of parameters considered in Table 4. All three values of the O-Si distance are within the allowable limits but the value 1.704Å, corresponding to the parameters 0.035, 0.04 and 0.65, agrees most closely with the Si-O distance, 1.70 Å, calculated from Goldschmidt's set of ionic radii and gives a further check on the oxygen parameters chosen for plazolite.

SUMMARY

The structure of plazolite is similar to that of grossularite. The lattice constant, 12.14±0.01 Å, is slightly larger than that of grossularite. There are 8 "molecules" in the body centered unit cube.

An atomic arrangement in the space group O_h^{10} has been found for plazolite which satisfactorily accounts for the diffraction data. The arrangement,

16 Al in 16(*a*) 000;
24 Ca in 24(*c*) $\frac{1}{4}$ $\frac{1}{8}$ 0;
16 Si in 24(*d*) $\frac{1}{4}$ $\frac{3}{8}$ 0;
96 O and OH in 96(*h*), xyz; x 0.035
y 0.04
z 0.65,

may be described as a defective garnet structure in which the Si is distributed at random over two thirds of a 24-fold position and O^{-2} and OH^- share a 96-fold position in the ratio two to one.

NOTES AND NEWS

THE TREND OF MINERALOGICAL RESEARCH

W. A. Tarr, *University of Missouri, Columbia, Missouri.*

The presidential address of Professor Winchell to the Mineralogical Society of America on December, 1932, was entitled "The New Mineralogy."[1] He contrasted the character of mineralogical studies in 1932 with those of three decades earlier and found that interest had shifted from surfaces and average composition of minerals to their internal structure and variations of composition.

The writer has been interested in the trend of research dealing primarily with the *origin* of minerals, and has classified the contents of *The American Mineralogist* and *The Mineralogical Magazine* for the last two decades, under various subject headings, such as crystallography, physical properties, x-ray and crystal structure, origin, chemical mineralogy, descriptive mineralogy, petrology, and new minerals; 10 headings in all. It is recognized that these subdivisions are not the only ones that might have been chosen, but all represent common subjects and cover the material fairly well. A really difficult task was the attempt to evaluate papers that included a wide range of material, an attempt which I am sure both Dr. Hunt and Dr. Spencer, editors respectively of the two magazines, would agree verged upon hopelessness. When such decisions were required, the article was placed in that group with which the major part of its subject matter was concerned. Only in the matter of "origin" was a *part* of an article culled out and classified differently from the main subject with which the article dealt. This was done in order to determine with some degree of accuracy the exact amount of space devoted to this significant subject.

As the study was made in order to note the trends of research, some preliminary graphs showing the distribution by volumes or years were made, but as they revealed nothing of importance in this connection, their use was abandoned. The percentages (in terms of pages) of each subject alone were used. As *The Mineralogical Magazine* incorporated its "reviews and abstracts" in a separate volume after 1920, these subjects were omitted in the study for both journals. Papers on the subject of "petrology" were first accepted by the American Mineralogical Society for their journal in 1932, whereas the British Mineralogical Society had always accepted them, hence the greater percentage of such subject matter in the magazine of the latter.

Not all the articles dealing with mineralogy necessarily find their way into the columns of these two journals; for example, many articles in magazines dealing with ore deposits contain much excellent mineralogical material, as the study of ore deposits is merely applied mineralogy, and *The American Journal of Science* has much excellent material on the origin of minerals. However, the material in the mineralogical journals can certainly be taken as indicating the type of studies being carried on by those interested in mineralogy and affiliated subjects.

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[1] Winchell, A. N., The new mineralogy: *Am. Mineral.*, vol. **18**, pp. 81–90, 1933.

In the graph showing the percentage amounts for each subject the values for both journals were placed together in order to show how surprisingly similar is the work being done in each country. That both journals show almost identical amounts (over 36 per cent) of descriptive material is surprising. The other subjects (save "origin," to be discussed below) need no comment.

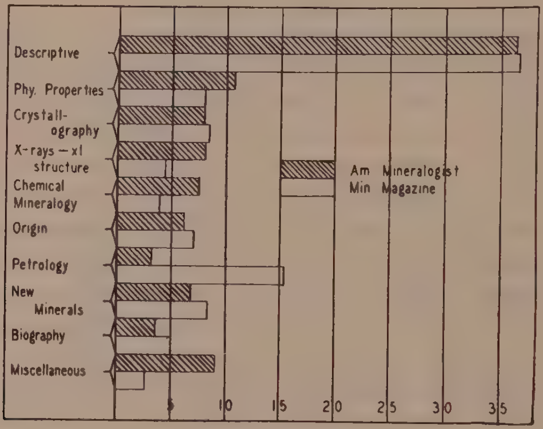

FIG. 1. The distribution of the contents of *The American Mineralogist and The Mineralogical Magazine* in percentages of pages of each subject from 1915 to 1935.

The writer was surprised at the similarity in the percentage amounts of the material dealing with origin and that devoted to x-ray studies, crystallography, chemical mineralogy, and physical properties. Yet in view of the great importance of origin and its bearing upon the interpretation of the other factors about a mineral, this percentage is too small. Discussions of "origin" occur more frequently in *The American Mineralogist* than in *The Mineralogical Magazine*, though many of such American contributions consist of only a short paragraph in a long and informative paper, whereas the British discussions are usually full and important articles on the subject. The frequent references to origin in *The American Mineralogist* are worth while, as they keep the subject before us.

The discussions of the origin of minerals varied widely in their manner of approach. Only a very few were actually determinative, *i.e.*, the mode of origin as established experimentally. Relatively little mineralogical research appears to be in progress in this very vital and essential field of determinative work largely because, in this country, of a lack of proper technical training on the part of the workers and a paucity of equipment. Physical plants for thorough experimental work in mineralogy are so lacking in the United States that the Geophysical Laboratory in Washington is the heaven of the ardent mineralogical research student. The majority of discussions of origin in the magazines were deductive, the origin being deduced from the background of facts exhibited by the occurrence of the mineral or minerals. This method calls not only for a very thorough knowledge of the science of mineralogy but also of the closely related sciences, chemistry and physics. Were the experimental method united with the deductive, the contribution so produced would have a maximum of value. Some of the discussions of origin are interpretations based upon the conditions of occurrence, a minimum of deduction being brought into the picture. Lastly, there are "opinions" of origin, about which the least said the better, although the majority of these doubtless represent "honest" opinions. And, lest anyone ascribe to these remarks a criticism of the editorial policy of the journals, allow me to say that nothing could be further from my mind, and I venture to say that few of us realize how much the tact of these editors enables them to keep "opinions" from their journals.

In conclusion, I am venturesome enough to say that experimental research on the origin of minerals is still largely an unexplored field. We need men with a technical training in chemistry and a background of experience in mineralogy. Such men must be forthcoming; and yet the well trained man is useless without the physical equipment with which to carry on the work. How few universities have departments of mineralogy with as fully equipped plants for research as have their departments of physics and chemistry. And why should this be so? Surely, an understanding of the components of the earth is as badly needed as that of the neutron and the cosmic ray—and yet the difference in the money spent on research in each! We in mineralogy are doing much, deductively, but we need to be doing more than 1/14 of our mineralogical research work on the origin of minerals.

MINERALOGY OF THE VIRGINIA DIABASE

Arthur A. Pegau, *University of Virginia.*

The diabase in Virginia is of a relatively simple composition being made up predominantly of two minerals, labradorite and augite. A careful study of the literature, however, has shown that at least forty-five other minerals have been reported as occurring in this rock type. The purpose of this article is to enumerate them and to show how diabase from various parts of the state differs in the number and variety of minerals.

The literature from which this information has been obtained has been secured from three sources.

(1) Bulletins of the *Virginia Geological Survey*, of which the one by Roberts[1] was especially helpful.

(2) Articles in journals and magazines, such as the one by Shannon.[2]

(3) Theses presented for the masters degree, by students in the School of Geology of the University of Virginia.

The occurrences of diabase in Virginia may be most conveniently discussed by grouping them into three divisions based upon the type of rock or rocks into which they have been introduced.

The three divisions or types of enclosing rocks are:

(1) Triassic sediments occurring within the boundaries of the Piedmont Province.

(2) Rocks of both igneous and metamorphic character, of Paleozoic and pre-Cambrian age, within the Piedmont Province.

(3) Paleozoic sediments in the Valley Province.

The greatest number of minerals, namely thirty-eight, have been reported as occurring in the diabase that intrude rocks of Triassic age. There are two possible explanations for the relatively greater number of minerals here.

(1) The diabase is nearest the original source and shows a greater degree of differentiation.

(2) Hydrothermal action has been more extensive here than elsewhere.

The two chief minerals here are labradorite and augite. Other primary minerals are albite, orthoclase, quartz, diopside, hypersthene, olivine, biotite, hornblende and the accessory constituents magnetite, ilmenite, apatite, and zircon. The following minerals, of hydrothermal origin, have been reported: Hornblende (variety byssolite), chlorite, diabanite

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[1] Roberts, J. K., The geology of the Virginia Triassic: *Va. Geol. Surv., Bull.* **29**, pp. 43–64, 1928.

[2] Shannon, Earl V., The mineralogy and petrology of intrusive diabase at Goose Creek, Loudoun County, Virginia: *Proc. U. S. National Museum*, vol. **66**, Article 2, 1924.

(a chloritic aggregation of minerals), epidote, calcite, sericite, titanite, prehnite, datolite, chabazite, stilbite, laumontite, apophylite, thaumosite, xonotlite, opal, paragonite, axinite, kaolinite, and the sulphides pyrite, chalcopyrite, galena and sphalerite. The products of weathering include limonite and kaolin.

The next greatest number of minerals are found in those dikes that intrude rocks of igneous and metamorphic character, of Paleozoic and pre-Cambrian age occurring in the Piedmont Province. The total number of minerals found in these dikes is twenty-three. The relatively greater number of dikes intruding this class of rocks may account for the large variety of minerals occurring within them.

The chief minerals in these dikes are again labradorite and augite, usually with either olivine or quartz and orthoclase, the latter two forming intergrowths. Other primary minerals, in subordinate or accessory amounts, include biotite, magnetite, ilmenite, rutile, pyrite, pyrrhotite, apatite and graphite. The following secondary minerals have been reported: hornblende, chlorite, serpentine, epidote, zoisite, calcite, sericite, leucoxene, limonite and kaolinite.

The minerals, eighteen in number, occurring in the diabase dikes of the Valley is less than in either of the other two occurrences. The reasons for this relatively smaller number may be two:

(1) These deposits are farthest from the original source.

(2) The number of dikes is the smallest.

Labradorite and augite, here as elsewhere, are the predominant constituents. Olivine is almost universally present, while quartz is rarely so. Other primary minerals usually in small amounts include: Analcite, magnetite, ilmenite, pyrite, apatite, orthoclase and a spinel, probably pleonaste. The secondary minerals found in these dikes include: Hornblende, epidote, chlorite, serpentine, iddingsite, titanite, kaolinite and limonite.

There has been a total of forty-seven minerals reported as occurring in the diabase rock in Virginia. The three minerals, nepheline, muscovite and an unidentified zeolite have been reported as occurring in rocks of Triassic age in the Valley Province, that were not of basaltic composition. Since the diabase dikes are also of Triassic age, this makes a total of fifty minerals that occur in rocks of Triassic age in Virginia.

Fifteen minerals as reported, are common to each of the three classes of dikes. Seventeen minerals are peculiar to the diabase occurring within the areas of Triassic sediments. The minerals albite, diopside and hypersthene have been the result of a more thorough differentiation of the diabase. The other minerals are products of hydrothermal action.

Only three minerals have been reported as occurring exclusively in dikes that intrude rocks of the second class. These three minerals, rutile, graphite and pyrrhotite, were found in diabase occurring within the rutile area near Roseland.

Analcite, iddingsite and pleonaste have been reported only from the Valley dikes. Work being done in the School of Geology at the University of Virginia at the present time has revealed the presence of pigeonite in some of the Valley diabases. Further studies may show that it is not an uncommon mineral in the Virginia diabase.

A Statement from the University of Pennsylvania, Bureau of Publicity

Establishment of a new four-year course in the Earth Sciences, made possible through a cooperative arrangement involving the University of Pennsylvania and the Academy of Natural Sciences of Philadelphia, has been announced in a joint statement issued by the two institutions.

The course will be offered for the first time with the opening of the University's academic year in the fall and will bring together two of the oldest learned foundations in America in the conduct of a program of teaching and research in geology, paleontology, and mineralogy.

Students enrolling will be registered as students of the University of Pennsylvania and the successful completion of the course will lead to the degree of bachelor of arts, granted by the University.

Instructional work will be carried on by a teaching and research staff comprising the present faculty of the Department of Geology and Mineralogy at the University, and members of the staff of the Department of Paleontology and Geology at the Academy of Natural Sciences.

In addition, it is the intention to make use of the invaluable scientific collections and other facilities of the Academy as well as those of the University's Department of Geology and Mineralogy.

The new curriculum is designed to serve students who desire opportunity for systematic study and research in one of the great groups of modern science as part of a well-balanced cultural education.

In accord with that objective a comprehensive undergraduate training in the ground work of geology, paleontology and mineralogy will be offered, as well as basic training in geological field work and mapping which is essential to prepare students for advanced survey and exploration in the field of the earth sciences.

Another phase of the instructional program now being developed will provide for advanced graduate study to be carried on through the joint facilities of the two institutions.

Thus, through its broad nature, the entire project will, it is hoped, bring about a closer coordination between fields of research such as paleo-archaeology, anthropology, and the study of early man and of human migration, which are dependent for some of their results upon research in geology, paleontology, and related subjects.

Representing the Academy of Natural Sciences on the teaching staff will be a group of widely known professional scientists now connected with that institution.

Among that group are Dr. Benjamin F. Howell, associate curator of paleontology and geology at the Academy, and associate professor of geology and paleontology at Princeton

University; Dr. Edwin H. Colbert, associate curator of vertebrate paleontology at the Academy and assistant curator of vertebrate paleontology at the American Museum of Natural History; Dr. Edgar B. Howard, acting curator of paleontology and geology at the Academy, and Dr. Hellmut deTerra, associate curator of Asiatic prehistory at the Academy and research associate of the Carnegie Institution in Washington.

Dr. Frederick Ehrenfeld, professor of geology and mineralogy at the University of Pennsylvania, will have general direction of the work of the four-year course.

PROCEEDINGS OF THE SOCIETIES

NEW YORK MINERALOGICAL CLUB

American Museum of Natural History, New York City, May, 19, 1937

The regular May meeting was called to order by the president with 85 members and guests present. The speaker of the evening was Prof. Arthur P. Honess, of Pennsylvania State College, who addressed the club upon "Etch Figures and their Significance in the Classification of Crystalline Structures." His recent work with optically active solvents, particularly with reference to their interesting effects in the etching of calcite was described with illustrative slides. Calcite was used because of its adaptability to work of this sort. *X*-ray work has shown calcite to possess a lower grade of symmetry than morphological studies would indicate, and the figures developed through the use of laevo-malic and dextro-malic acids have born out this low grade symmetry. Figures upon adjoining scalenohedral faces were entirely dissimilar. The symmetry derived by Dr. Honess would place calcite in the quartz class, with one axis of three-fold and three of two-fold symmetry. This difference may be explained by the difference in the direction of the C-O bonds in successive layers on the rhombohedral plane, developed by the differential, directional attack of the optically active solvent. Full symmetry is obtained in etching with inactive acids, and the asymmetry of the figures appears to be a function of the concentration of the optically active ions. Different solvents and different concentrations give different figures, but the same symmetry may be seen in all. A dextro-acid reverses the figures obtained from a laevo-acid.

Other minerals were studied with similar results. Smithsonite agrees with calcite. Dolomite, already lower morphologically, gives such different figures above and below that the mineral appears to be hemimorphic, when etched with laevo-malic acid in NaOH. Hemimorphite lacks even the vertical plane of symmetry obtained in etching with optically inactive solvents. Continued work with such solvents should make it possible to determine crystal structures from the symmetries on the different forms, but the work is still in its elementary stage.

F. H. Pough, *Secretary*

NEW MINERAL NAMES

Ferri-sicklerite

Percy Quensel: Minerals of the Varuträsk Pegmatite. I. The Lithium—Manganese Phosphates. *Geol. Fören. Förhandl.*, vol. **59**, pp. 82–86, 1937.

Name: From its relationship to sicklerite.

Chemical Properties: A phosphate of manganese and iron: $12\ RO\cdot 5Fe_2O_3\cdot 9P_2O_5$ (where $R = Mn''$ and Li). Analyses (by Miss Thelma Berggren).

	1. Zone surrounding triphyllite	2. Lövlunden farm
Insol.	1.66	2.42
$H_2O-105°$	0.51	0.79
$H_2O+105°$	0.51	0.44
Fe_2O_3	27.20	29.08
Mn_2O_3	0.00	—
Al_2O_3	0.00	0.00
FeO	0.59	0.22
MnO	19.13	15.20
CaO	1.36	1.88
MgO	0.11	1.70
Li_2O	3.72	3.26
Na_2O	0.81	0.88
K_2O	0.00	0.00
P_2O_5	44.80	44.64
	100.40	100.51

Physical and Optical Properties: Color, dark brown; streak, brown to reddish brown. Under the microscope, deep reddish brown and almost nonpleochroic. *n* higher than 1.78. G.=3.271–3.391.

Occurrence: Found as an alteration rim about triphyllite. In the change ferrous iron becomes ferric, manganese remains unchanged, without altering the ratios. A further alteration in which the Mn'' becomes Mn''' yields the species heterosite. From Varuträsk, near Boliden, Sweden.

Mn-sicklerite is the term applied to the manganese sicklerite derived from lithiophilite.

W. F. Foshag

Varulite

Percy Quensel: *Ibid.*, pp. 93–95.

Name: From the locality Varuträsk (*Varu* marsh or lake).

Chemical Properties: A phosphate of sodium, manganese and iron; $Na_2O \cdot 5(Mn,Fe,Ca)O.2\,P_2O_5$. Analysis: Insol. 1.80, $H_2O-105°$ 0.14, $H_2O+105°$ 0.75, Fe_2O_3 8.35, Al_2O_3 0.36, FeO 7.52, MnO 25.30, CaO 4.86, MgO 0:00, Li_2O 0.88, Na_2O 7.12, K_2O 0.12, P_2O_5 42.80, F_2 0.06; total 100.06.

Physical and Optical Properties: Color, dull olive green; under the microscope, colorless. Biaxial, $2V=70°$. Dispersion distinct, $r>v$. Plane of the optic axes vertical to the best cleavage. $\alpha=1.720$, $\gamma=1.732$. Two well marked cleavages at right angles. G=3.581.

Occurrence: Found as fine granular masses associated with alluaudite, tourmaline and lepidolite at Varuträsk, near Boliden, Sweden. The material is slightly altered.

W. F. F.

Headdenite
Na-heterosite
Na-purpurite

Percy Quensel: *Ibid.*, pp. 95–96.

The phosphate near triphyllite described by Headden (Dana, p. 758) is provisionally named headdenite.

Na-heterosite and Na-purpurite are theoretical heterosite and purpurite derived from headdenite and varulite instead of from triphyllite and lithiophilite. They would differ in no essential respect from the normal minerals except in origin.

W. F. F.